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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q77065

Makoto MOMOTA

Appln. No.: 10/642,576

Group Art Unit: 1752

Filed: August 19, 2003

Examiner: THORNTON, YVETTE C

For: POSITIVE PHOTORESIST COMPOSITION

STATEMENT

Commissioner for Patents
Alexandria, Virginia 22313-1450

Sir/Madam:

I, Hidetaka Ota, do declare and state that:

I graduated from Osaka University, Faculty of Engineering Science, Department in Chemical Science and Engineering, having received a Master's Degree of in March, 1998.

I am presently employed by NGB CORPORATION of Tokyo, Japan and have been so employed since April, 1998.

I understand the Japanese and English languages. The attached English document is an accurate English translation made by me of Japanese Patent Application No. 2002-241946, filed August 22, 2002, upon which the above-identified U.S. patent application claims a priority.

Date : December 16, 2004

Name :

A handwritten signature in black ink, appearing to be "Hidetaka Ota".

Hidetaka Ota



[Designation of Document] Specification

[Title of the Invention] POSITIVE PHOTORESIST COMPOSITION

[Claims]

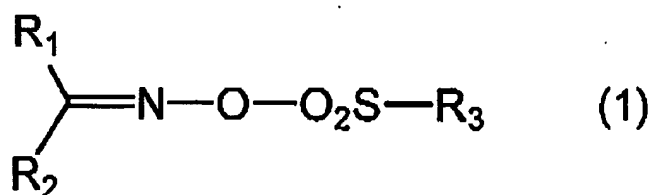
[Claim 1] A positive photoresist composition which comprises:

(A) an oxime sulfonate compound represented by the following general formula (1),

(B) a resin which has structural units represented by the following general formula (X) and which decomposes by the action of an acid and comes to have enhanced solubility in an alkaline developing solution, and

(C) a fluoroaliphatic-group-containing polymeric compound containing repeating units derived from a monomer represented by the following general formula (2):

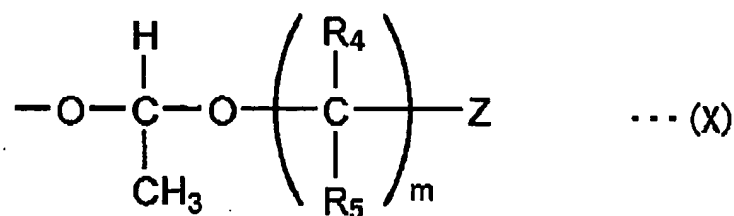
[Ka-1]



wherein R_1 and R_2 each independently represent an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, or a cyano group, provided that R_1 and R_2 may be bonded to each other to form a ring, and R_3 represents an alkyl group or an aryl group, and

R₁ and R₂ each may be bonded, through a single bond or a connecting group, to the R₁ or R₂ of another compound represented by general formula (1);

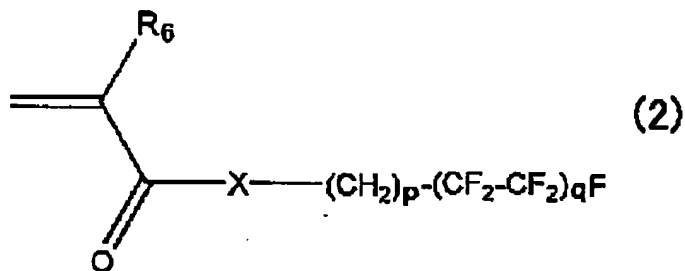
[Ka-2]



wherein R₄ and R₅ each independently represent a hydrogen atom or an alkyl group, Z represents an alkyl group, and

m represents an integer of 1 to 20;

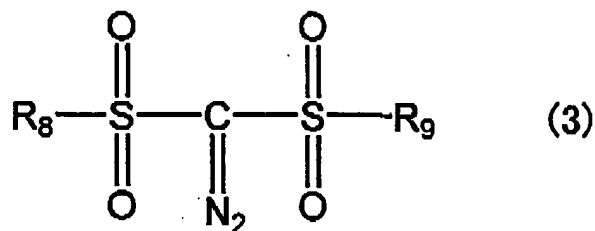
[Ka-3]



wherein R₆ represents a hydrogen atom or a methyl group, X represents an oxygen atom, a sulfur atom, or -N(R₇)-, p represents an integer of 1 to 6, and q represents an integer of 2 to 4, provided that R₇ represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[Claim 2] The positive photoresist composition of claim 1, which further contains a compound represented by the following general formula (3) which generates an acid upon irradiation with actinic rays or a radiation:

[Ka-4]



wherein R₈ and R₉ each independently represents an alkyl group or an aryl group.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a positive photoresist composition for use in producing semiconductor integrated-circuit elements, masks for integrated circuit production, printed wiring boards, liquid-crystal panels, or the like.

[0002]

[Prior Art]

Chemical amplification type positive resist compositions are pattern-forming materials which, when irradiated with a radiation such as, e.g., far ultraviolet rays, generate an

acid in the exposed areas and come to have a difference in solubility in a developing solution between the areas irradiated with the actinic radiation and the unirradiated areas as a result of a reaction catalyzed by the acid to thereby form a pattern on the substrate.

[0003]

Surfactants are generally incorporated into such chemical amplification type resist compositions in order to eliminate striations and the like and improve applicability.

Examples of the surfactants in general use include nonionic surfactants such as polyoxyethylene alkyl ethers,

polyoxyethylene alkylaryl ethers,

polyoxyethylene/polyoxypropylene block copolymers, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters, and further include fluorochemical surfactants,

organosiloxane polymers, and acrylic acid or methacrylic acid (co)polymers. In JP-B-7-21626 is disclosed a resist

composition for semiconductor microfabrication which comprises an alkali-soluble resin, an organic solvent containing at least a monohydroxy monocarboxylic acid ester, a fluorochemical surfactant, and a radiation-sensitive substance. Furthermore,

JP-A-7-246873 discloses a chemical amplification type photoresist composition employing a combination of a solvent of a specific structure and a fluorochemical surfactant, while JP-A-2000-162768 discloses one employing a fluorochemical

surfactant having a specific structure.

[0004]

With the recent trend toward scale down and higher throughputs, it has become important to diminish errors caused by exposure. However, the resists of the related art described above have a problem concerning defect generation during development and this has resulted in a considerable decrease in yield.

[0005]

[Problems that the Invention is to Solve]

Accordingly, an object of the invention is to provide a positively photosensitive composition which is effective in considerably diminishing development defects.

[0006]

[Means for Solving the Problems]

The invention provides a positively photosensitive composition having the following constitutions, with which that object of the invention is accomplished.

Namely, the positive photoresist composition according to the invention has the following constitutions.

[0007]

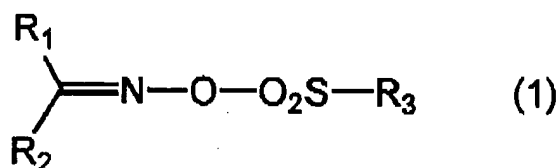
- (1) A positive photoresist composition which comprises:
 - (A) an oxime sulfonate compound represented by the following general formula (1),
 - (B) a resin which has structural units represented by the

following general formula (X) and which decomposes by the action of an acid and comes to have enhanced solubility in an alkaline developing solution, and

(C) a fluoroaliphatic-group-containing polymeric compound containing repeating units derived from a monomer represented by the following general formula (2):

[0008]

[Ka-5]



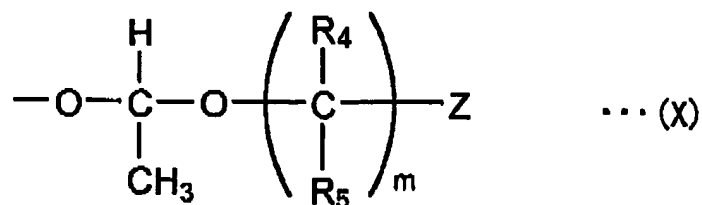
[0009]

wherein R_1 and R_2 each independently represent an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, or a cyano group, provided that R_1 and R_2 may be bonded to each other to form a ring, and R_3 represents an alkyl group or an aryl group, and

R_1 and R_2 each may be bonded, through a single bond or a connecting group, to the R_1 or R_2 of another compound represented by general formula (1);

[0010]

[Ka-6]

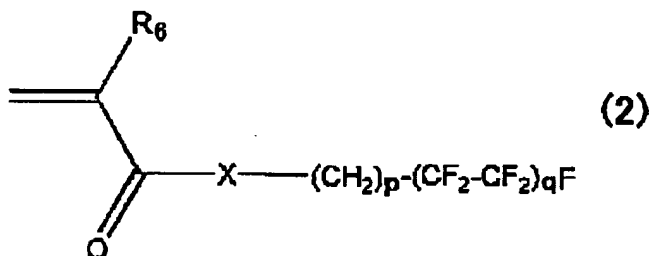


[0011]

wherein R_4 and R_5 each independently represent a hydrogen atom or an alkyl group, Z represents an alkyl group, and m represents an integer of 1 to 20;

[0012]

[Ka-7]



[0013]

wherein R_6 represents a hydrogen atom or a methyl group, X represents an oxygen atom, a sulfur atom, or $-N(R_7)-$, p represents an integer of 1 to 6, and q represents an integer of 2 to 4, provided that R_7 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

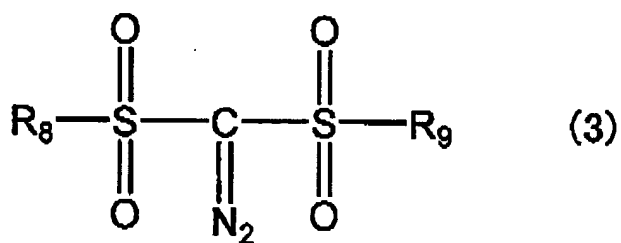
[0014]

(2) The positive photoresist composition as described in (1) above which further contains a compound represented by the

following general formula (3) which generates an acid upon irradiation with actinic rays or a radiation:

[0015]

[Ka-8]



[0016]

wherein R₈ and R₉ each independently represents an alkyl group or an aryl group.

[0017]

[Mode for Carrying Out the Invention]

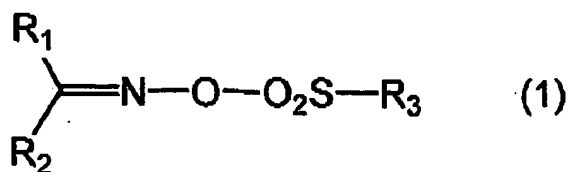
The invention will be explained below in detail.

[0018]

[1] Compound Represented by General Formula (1) Generating Acid upon Irradiation with Actinic Rays or Radiation (Photo-Acid Generator)

[0019]

[Ka-9]



[0020]

The compound represented by general formula (1) is a compound (photo-acid generator) which generates an acid when irradiated with actinic rays or radiation for use in patterning, such as, e.g., KrF excimer laser light, ArF excimer laser light, or electron beams.

In general formula (1), R₁ and R₂ each independently represent an alkyl group, alkenyl group, alkynyl group, aryl group, heterocyclic group, or cyano group, provided that R₁ and R₂ may be bonded to each other to form a ring. R₃ represents an alkyl or aryl group.

R₁ and R₂ may be bonded, through a single bond or connecting chain, to the R₁ or R₂ of another compound represented by general formula (1).

[0021]

Groups R₁ and R₂ each preferably have 1 to 16 carbon atoms and may have one or more substituents.

Group R₃ preferably has 1 to 16 carbon atoms, more preferably 2 to 12 carbon atoms, and may have one or more substituents.

The alkyl groups represented by R_1 , R_2 , and R_3 may be linear, branched, or cyclic, and preferably are alkyl groups having 1 to 16 carbon atoms. Examples of the linear or branched alkyl groups include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, t-amyl, n-hexyl, n-octyl, isooctyl, n-decyl, undecyl, dodecyl, and hexadecyl, and further include trifluoromethyl, perfluoropropyl, perfluorobutyl, perfluoro-t-butyl, perfluorooctyl, perfluoroundecyl, and 1,1-bis(trifluoromethyl)ethyl.

The cycloalkyl groups each preferably have 3 to 8 carbon atoms. Examples thereof include cyclopropyl, cyclopentyl, and cyclohexyl.

[0022]

The alkenyl groups represented by R_1 and R_2 may be linear, branched, or cyclic, and preferably are alkenyl groups having 2 to 16 carbon atoms. Examples of the linear or branched alkenyl groups include allyl, methallyl, vinyl, methylallyl, 1-butenyl, 3-butenyl, 2-butenyl, 1,3-pentadienyl, 5-hexenyl, 2-oxo-3-pentenyl, decapentenyl, and 7-octenyl.

Examples of the cyclic alkenyl groups include cyclobutenyl, cyclohexenyl, cyclopentadienyl, and bicyclo[4.2.4]dodeca-3,7-dien-5-yl.

[0023]

The alkynyl groups represented by R_1 and R_2 each preferably have 2 to 16 carbon atoms. Examples thereof include ethynyl,

propargyl, 2-butyryl, 4-hexynyl, 2-octynyl, phenylethynyl, and cyclohexylethynyl.

[0024]

The aryl groups represented by R_1 , R_2 , and R_3 each preferably have 5 to 16 carbon atoms. More preferred examples of the aryl groups include ones having 6 to 14 carbon atoms, such as phenyl, tolyl, methoxyphenyl, and naphthyl.

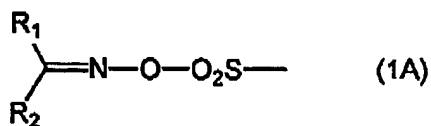
The heterocyclic groups preferably are ones having 5 to 15 carbon atoms. Examples thereof include the aforementioned aryl groups in which one or more of the ring-constituting atoms have been replaced by one or more heteroatoms. Specific examples thereof include thiophenefuryl and thienyl.

[0025]

Examples of the substituents which may be possessed by each of the groups described above include alkyl groups (e.g., the same alkyl groups as those which may be represented by R_1 , preferably ones having 1 to 4 carbon atoms), alkoxy groups (preferably ones having 1 to 4 carbon atoms, e.g., methoxy, ethoxy, hydroxyethoxy, linear or branched propoxy, and linear or branched butoxy), halogen atoms (e.g., fluorine, chlorine, and iodine), cyano, hydroxy, carboxy, nitro, aryloxy groups (preferably having 6 to 14 carbon atoms), alkylthio groups, aralkyl groups (preferably ones having 6 to 14 carbon atoms, e.g., benzyl and naphthylmethyl), and groups represented by the following general formula (1A).

[0026]

[Ka-10]



[0027]

In the formula, R_1 and R_2 have the same meanings as the R_1 and R_2 in general formula (1).

[0028]

R_1 and R_2 each may be bonded, through a single bond or a connecting chain, to the R_1 or R_2 of another compound represented by general formula (1). Namely, the compound represented by general formula (1) includes one having two or three oxime sulfonate structures bonded to each other through a connecting chain.

Examples of the connecting chain include alkylene chains (preferably having 1 to 10 carbon atoms), alkenylene chains (preferably having 1 to 10 carbon atoms), alkynylene chains (preferably having 1 to 10 carbon atoms), phenylene, furylene, thienylene, -O-, -S-, -N-, -CO-, and combinations of two or more of these.

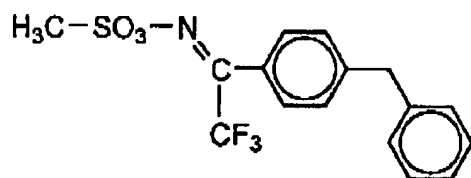
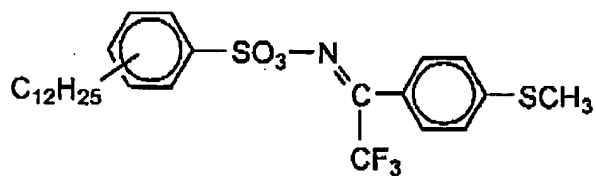
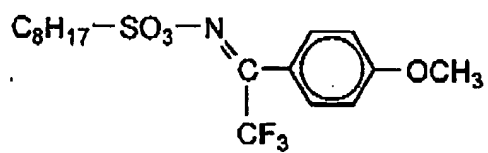
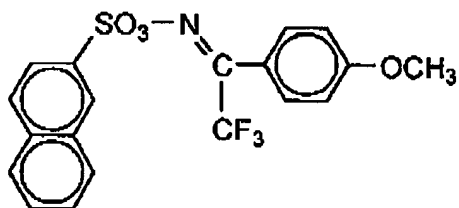
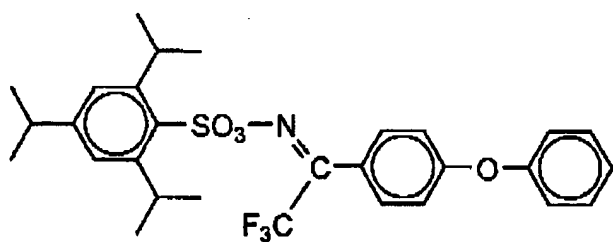
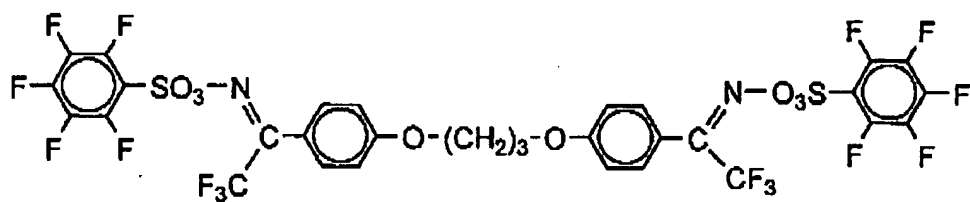
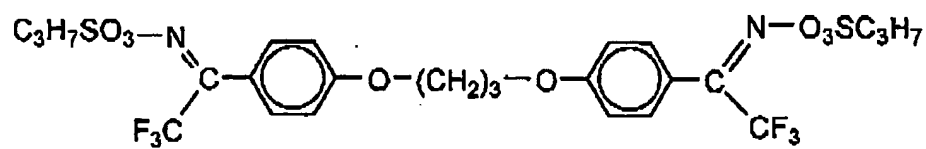
[0029]

Specific examples of the compound represented by general

formula (1) are shown below, but ingredient (A) in the invention should not be construed as being limited thereto.

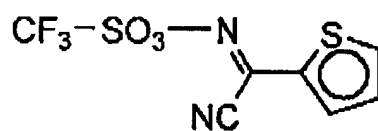
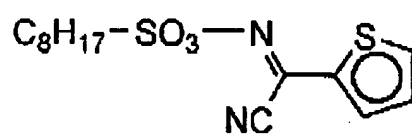
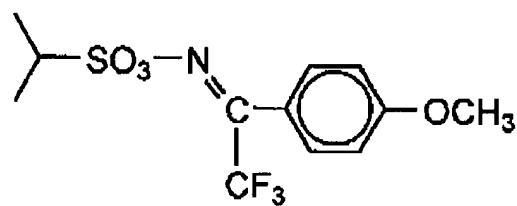
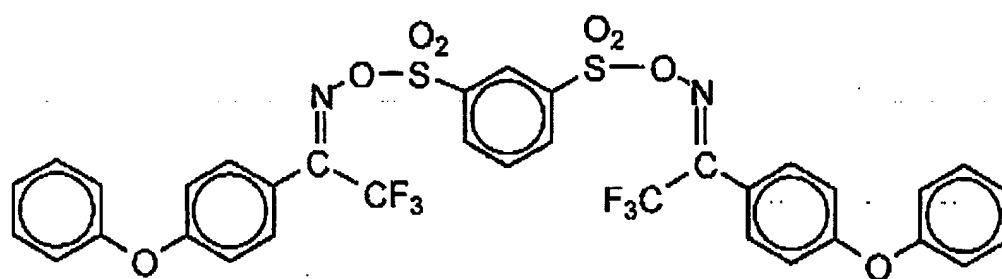
[0030]

[Ka-11]



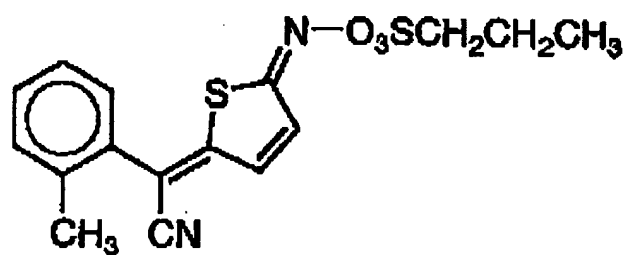
[0031]

[Ka-12]



[0032]

[Ka-13]



[0033]

The compound represented by general formula (1) to be used as ingredient (b) can be obtained, for example, by the method described in S.R. Sandler & W. Karo, *Organic Functional Group Preparations*, Vol.3, Academic Press. Specifically, the compound can be obtained by reacting a desired acid halide with an oxime compound synthesized, for example, by the reaction of a ketone with hydroxylamine or a salt thereof or by converting an "active" methylene group into a nitroso group with an alkyl nitrite or alkyl hydrogen nitrate.

[0034]

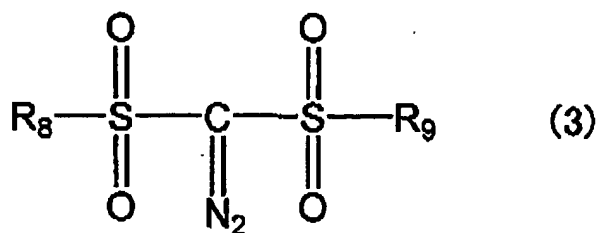
The amount of the compound represented by general formula (1) to be added is generally from 0.1 to 10% by weight, preferably from 0.25 to 8% by weight, more preferably from 0.5 to 4% by weight, based on the solid ingredients in the composition.

[0035]

[2] The resist composition of the invention preferably further contains a diazodisulfone compound represented by the following general formula (3) as a compound which decomposes upon irradiation with a radiation or actinic rays to generate an acid (photo-acid generator).

[0036]

[Ka-14]



[0037]

R₈ and R₉ each independently represent an alkyl or aryl group.

The alkyl groups represented by R₈ and R₉ may be linear, branched, or cyclic and may have one or more substituents. Preferred examples of the linear or branched alkyl groups include ones having 1 to 4 carbon atoms, such as methyl, ethyl, propyl, n-butyl, sec-butyl, and t-butyl.

Preferred examples of the cycloalkyl groups include ones having 3 to 8 carbon atoms, such as cyclopropyl, cyclopentyl, and cyclohexyl.

The aryl groups represented by R₈ and R₉ may have one or more substituents. Preferred examples thereof include ones having 6 to 14 carbon atoms, such as phenyl, tolyl, methoxyphenyl, and naphthyl.

[0038]

Examples of the substituents which may be possessed by the alkyl groups and aryl groups represented by R₈ and R₉ include alkoxy groups (preferably having 1 to 5 carbon atoms), halogen atoms (fluorine, chlorine, and iodine), cyano, hydroxy,

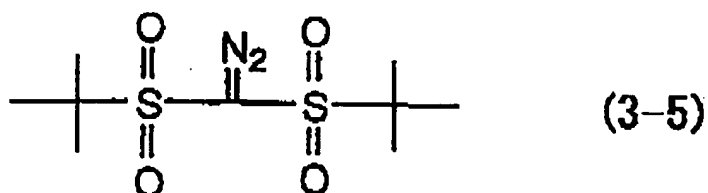
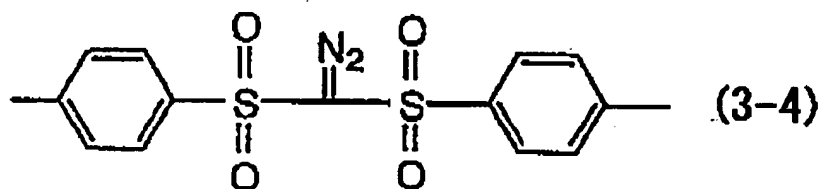
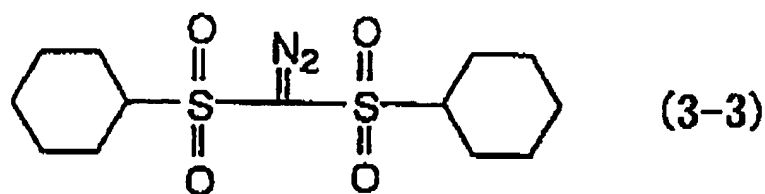
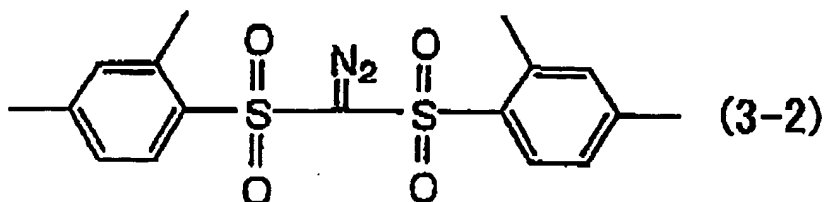
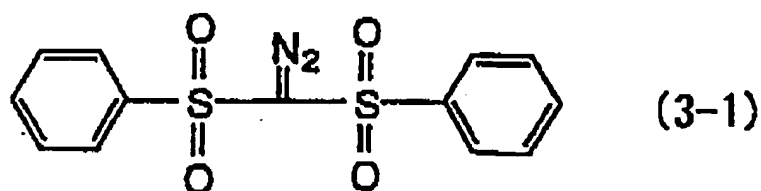
carboxy, and nitro. With respect to the aryl groups, examples of the substituents further include alkyl groups, examples of which include the same alkyl groups as enumerated above.

[0039]

Specific examples of the compound represented by general formula (3) are shown below, but this compound usable in the invention should not be construed as being limited thereto.

[0040]

[Ka-15]



[0041]

The compound represented by general formula (3) can be synthesized, for example, by the method disclosed in Japanese Patent No. 3,024,621 which comprises diazotizing bisulfonylemethane with toluenesulfonyl azide.

[0042]

The amount of the compound represented by general formula

(3) to be added, which generates an acid upon irradiation with actinic rays or a radiation, is generally from 0.01 to 7% by weight, preferably from 0.05 to 5% by weight, more preferably from 0.1 to 3% by weight, based on the solid ingredients in the composition.

[0043]

The proportion (by weight) of the compound represented by general formula (1) to the compound represented by general formula (3) is preferably from 90/10 to 15/85, more preferably from 80/20 to 20/80, especially preferably from 70/30 to 40/60.

[0044]

Other photo-acid generators may be used in the invention in combination with the photo-acid generators described above.

Such optional photo-acid generators for use in the invention can be suitably selected from photoinitiators for cationic photopolymerization, photoinitiators for free-radical photopolymerization, photodecolorants or optical color changers for dyes, known compounds for use in microresist production or the like which generate an acid upon irradiation with actinic rays or a radiation, and mixtures of two or more of these.

[0045]

Examples thereof include onium salts such as diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts, and arsonium salts,

organohalogen compounds, organometallic/organic halide combinations, photo-acid generators having an o-nitrobenzyl type protective group, and compounds which photodecompose to generate a sulfonic acid, represented by iminosulfonates.

[0046]

Such photo-acid generators capable of being used in combination with the specific photo-acid generators according to the invention may be incorporated in an amount of generally up to 80 parts by weight per 100 parts by weight of the sum of the photo-acid generators represented by general formula (1) and general formula (3).

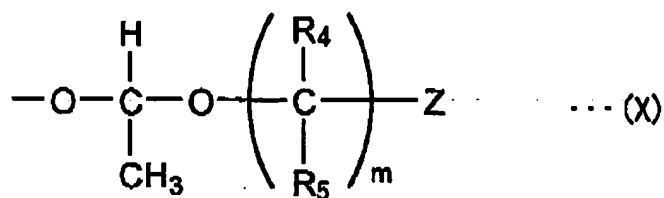
[0047]

[3] Resin Decomposing by the Action of Acid and Coming to Have Enhanced Solubility in Alkaline Developing Solution (Ingredient B)

The resist composition of the invention contains a resin which has structural units represented by general formula (X) as groups dissociating by the action of an acid (acid-dissociable groups) and which decomposes by the action of an acid and comes to have enhanced solubility in an alkaline developing solution.

[0048]

[Ka-16]



[0049]

In general formula (X), R_4 and R_5 each independently represent a hydrogen atom or an alkyl group. Z represents an alkyl group.

Symbol m represents an integer of 1 to 20.

[0050]

The alkyl groups represented by R_4 and R_5 may be linear, branched, or cyclic and may have one or more substituents.

The linear alkyl groups each have preferably 1 to 30, more preferably 1 to 20 carbon atoms. Examples thereof include methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, and n-decanyl.

The branched alkyl groups each have preferably 1 to 30, more preferably 1 to 20 carbon atoms. Examples thereof include isopropyl, isobutyl, t-butyl, isopentyl, t-pentyl, isohexyl, t-hexyl, isoheptyl, t-heptyl, isooctyl, t-octyl, isononyl, and t-decanoyl.

The cycloalkyl groups each have preferably from 3 to 30, more preferably 3 to 20 carbon atoms. Examples thereof include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl,

cycloheptyl, cyclooctyl, cyclononyl, and tetracyclododecanyl.

[0051]

The alkyl group represented by Z in general formula (X) may be linear, branched, or cyclic and may have one or more substituents.

[0052]

The linear or branched alkyl group preferably has 1 to 10 carbon atoms. Examples thereof include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-pentyl, isopentyl, t-pentyl, n-hexyl, isohexyl, t-hexyl, n-heptyl, isoheptyl, t-heptyl, n-octyl, isooctyl, t-octyl, n-nonyl, isononyl, t-nonyl, n-decanyl, isodecanyl, and t-decanyl.

The cycloalkyl group preferably has 3 to 8 carbon atoms. Examples thereof include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl.

[0053]

Examples of the substituents which may be possessed by the groups described above include hydroxy, halogen atoms (fluorine, chlorine, bromine, and iodine), nitro, cyano, the aforementioned alkyl groups, the aforementioned cycloalkyl groups, alkoxy groups such as methoxy, ethoxy, hydroxyethoxy, propoxy, hydroxypropoxy, n-butoxy, isobutoxy, sec-butoxy, and t-butoxy, alkoxycarbonyl groups such as methoxycarbonyl and ethoxycarbonyl, aralkyl groups such as benzyl, phenethyl, and cumyl, aralkyloxy groups, acyl groups such as formyl, acetyl,

butyryl, benzoyl, cinnamoyl, and valeryl, acyloxy groups such as butyryloxy, the aforementioned alkenyl groups, alkenyloxy groups such as vinyloxy, propenyloxy, allyloxy, and butenyloxy, aryloxy groups such as phenoxy, and aryloxycarbonyl groups such as benzoyloxy.

These substituents each may have one or more substituents.

[0054]

The resin having acid-dissociable groups described above is a compound which has a structure formed by incorporating acid-dissociable groups into a compound having a molecular-weight distribution and obtained by polymerizing one or more monomers and which becomes alkali-soluble by the action of an acid.

[0055]

The resin having acid-dissociable groups described above is a resin which has acid-dissociable groups on the main chain or side chains of the resin or on both the main chain and side chains. Preferred is a resin having acid-dissociable groups on side chains thereof.

[0056]

In the case where acid-dissociable groups are to be bonded as side chains to a base resin, this base resin may be an alkali-soluble resin having -OH or -COOH groups in side chains, preferably having $-R^0-COOH$ or $-Ar-OH$ groups as side chains.

In those groups, $-R^0-$ represents an optionally substituted, aliphatic or aromatic hydrocarbon group having a valence of 2 or higher, and $-Ar-$ represents an optionally substituted, monocyclic or polycyclic aromatic group having a valence of 2 or higher.

[0057]

A preferred base resin in the invention is an alkali-soluble resin having phenolic hydroxyl groups.

The alkali-soluble resin having phenolic hydroxyl groups to be used in the invention preferably is a copolymer containing at least 30% by mole, preferably at least 50% by mole, repeating units derived from o-, m-, or p-hydroxystyrene (these are inclusively referred to as hydroxystyrene) or from o-, m-, or p-hydroxy- α -methylstyrene (these are inclusively referred to as hydroxy- α -methylstyrene), or is a homopolymer of hydroxystyrene or hydroxy- α -methylstyrene or a resin obtained from the copolymer or homopolymer by partly hydrogenating the benzene nuclei of those units. More preferred is a p-hydroxystyrene homopolymer.

Preferred examples of the monomers usable besides hydroxystyrene and hydroxy- α -methylstyrene for producing the copolymer by copolymerization include acrylic esters, methacrylic esters, acrylamide and derivatives thereof, methacrylamide and derivatives thereof, acrylonitrile, methacrylonitrile, maleicanhydride, styrene, α -methylstyrene,

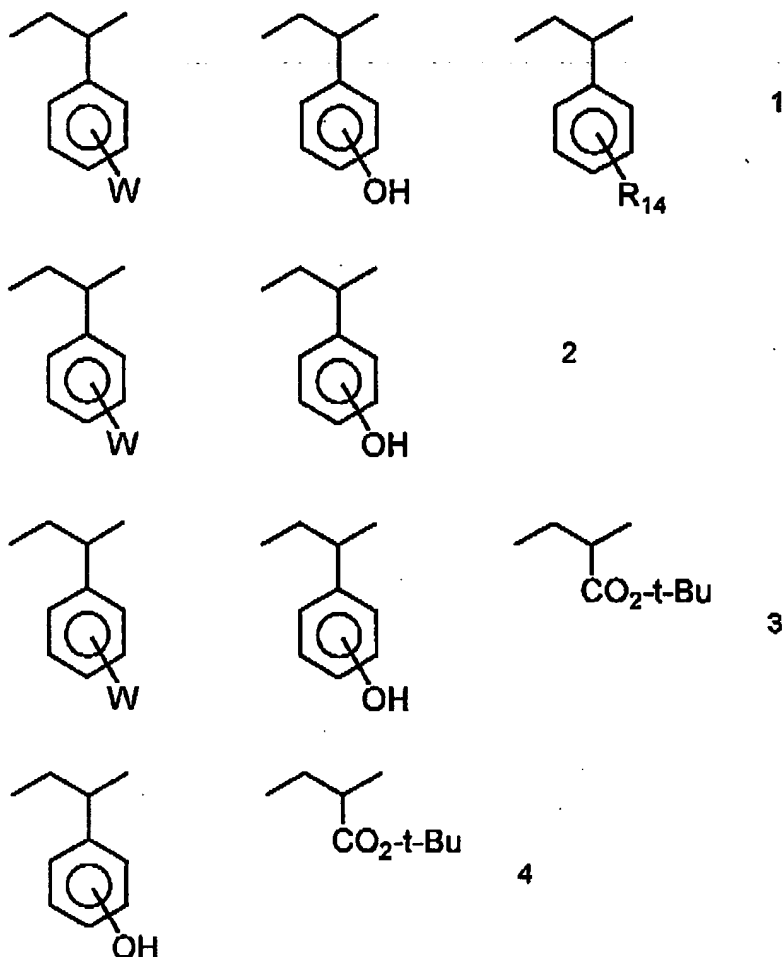
acetoxystyrene, alkoxystyrenes, and alkylstyrenes. More preferred are styrene, acetoxystyrene, and t-butylstyrene.

[0058]

Examples of preferred resins for use in the invention include the following ones. These resins can be especially advantageously used when a pattern is to be formed through exposure with a KrF excimer laser.

[0059]

[Ka-17]



[0060]

In the formulae given above, W represents an acid-dissociable group represented by general formula (X). R^{14} represents an acid-stable group.

[0061]

R^{14} , which is a group not dissociating by the action of an acid (referred to as an acid-stable group), represents a hydrogen atom, halogen atom, alkyl group, alkoxy group, or

acyloxy group.

Preferred examples of the alkyl group as the acid-stable group represented by R^{14} include alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, propyl, n-butyl, sec-butyl, and t-butyl.

[0062]

Preferred examples of the alkoxy group include alkoxy groups having 1 to 4 carbon atoms, such as methoxy, ethoxy, hydroxyethoxy, propoxy, hydroxypropoxy, n-butoxy, isobutoxy, and sec-butoxy.

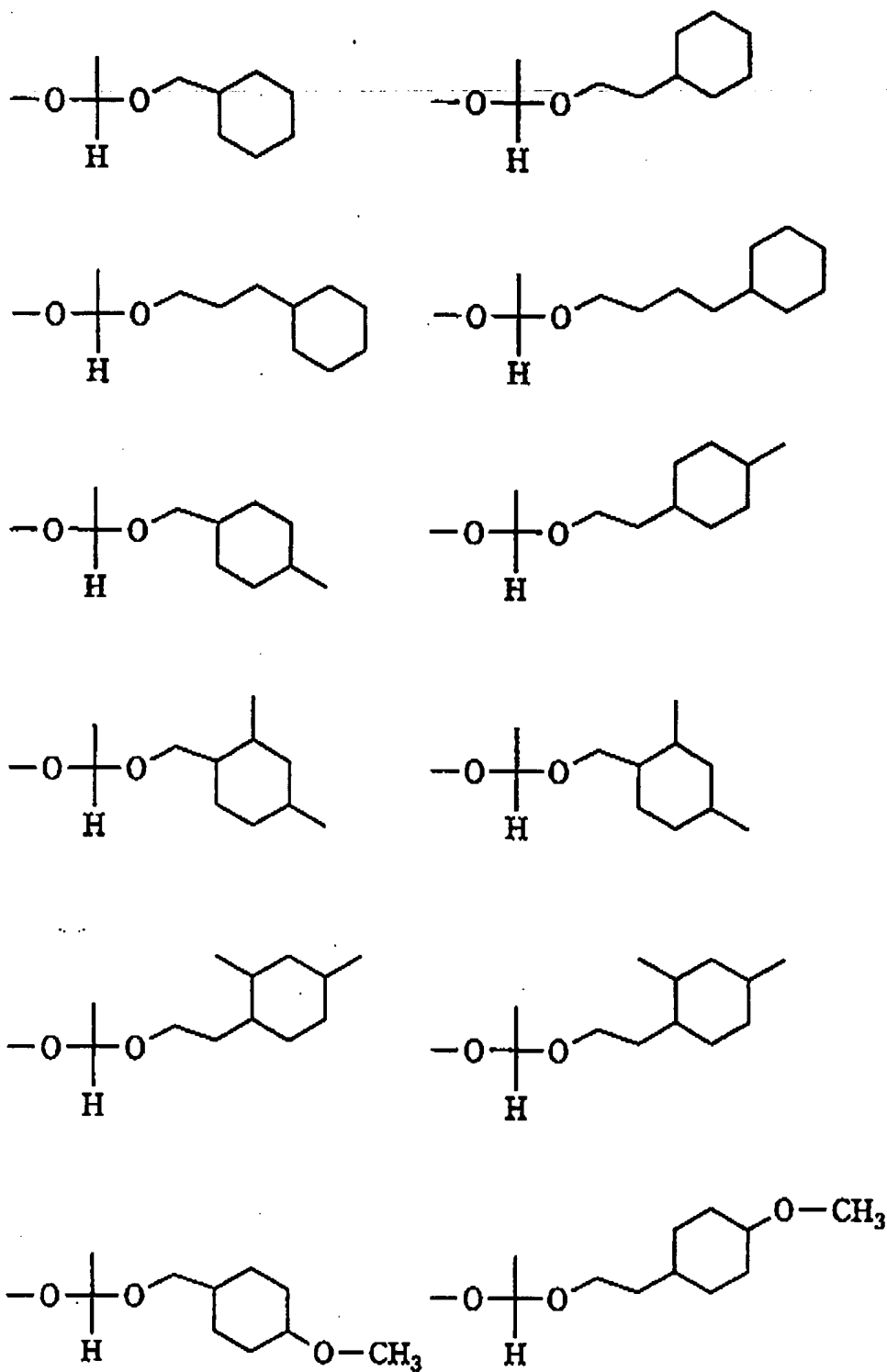
Preferred examples of the acyloxy group include ones having 2 to 7 carbon atoms, such as acetoxy, propanoyloxy, butanoyloxy, and benzoyloxy.

[0063]

Specific examples of the groups represented by general formula (X) are shown below, but the groups should not be construed as being limited to these examples.

[0064]

[Ka-18]



[0065]

In such a resin to be used in the invention, the content of the repeating units (structural units) having a group represented by general formula (X) is preferably from 5 to 50% by mole, more preferably from 5 to 30% by mole, based on all repeating units.

[0066]

The resin having groups represented by general formula (X) in the invention may contain other acid-dissociable groups besides the groups represented by general formula (X).

[0067]

The resin having groups represented by general formula (X) can be obtained by synthesizing the corresponding vinyl ether and reacting it by a known method with an alkali soluble resin containing phenolic hydroxyl groups which has been dissolved in an appropriate solvent, e.g., tetrahydrofuran.

This reaction is generally conducted in the presence of an acid catalyst, preferably an acid ion-exchange resin, hydrochloric acid, p-toluenesulfonic acid, or a salt such as pyridinium tosylate. The corresponding vinyl ether can be synthesized from an active starting material, such as chloroethyl vinyl ether, by a method such as, e.g., nucleophilic substitution reaction. It can be synthesized also with a mercury or palladium catalyst.

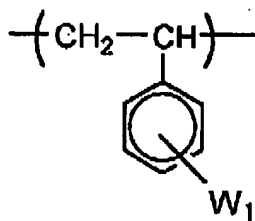
Another method usable for the synthesis comprises conducting acetal interchange using the corresponding alcohol and a vinyl ether. In this case, the substituent to be incorporated is possessed by the alcohol, and the vinyl ether to be caused to coexist therewith is a relatively unstable vinyl ether such as t-butyl vinyl ether. This reaction is conducted in the presence of an acid such as p-toluenesulfonic acid or pyridinium tosylate.

[0068]

Examples of the repeating units having a group represented by general formula (X) in the resin described above include structural units represented by the following general formula (VI).

[0069]

[Ka-19]



(VI)

[0070]

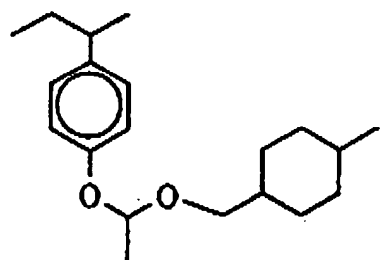
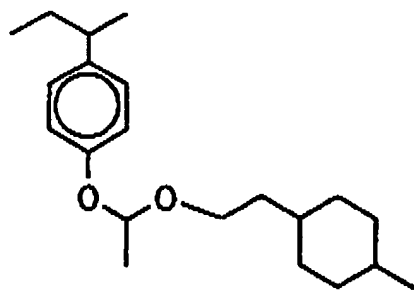
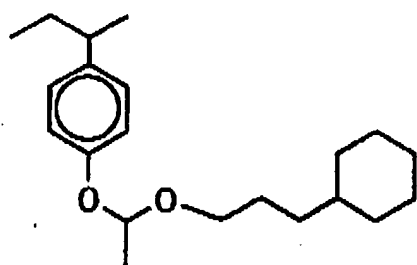
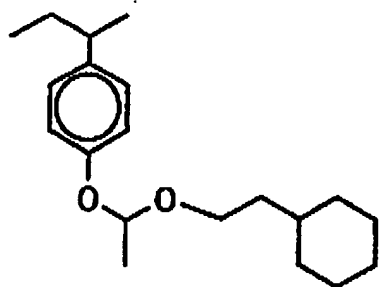
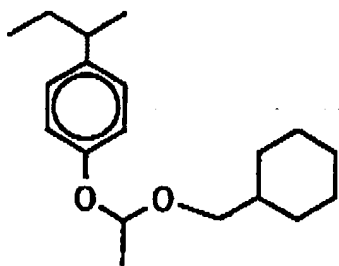
Substituent W_1 in general formula (VI) represents a group represented by general formula (X).

[0071]

Specific examples of the structural units represented by general formula (VI) are shown below, but the resin to be used in the invention should not be construed as being limited to ones having these structural units.

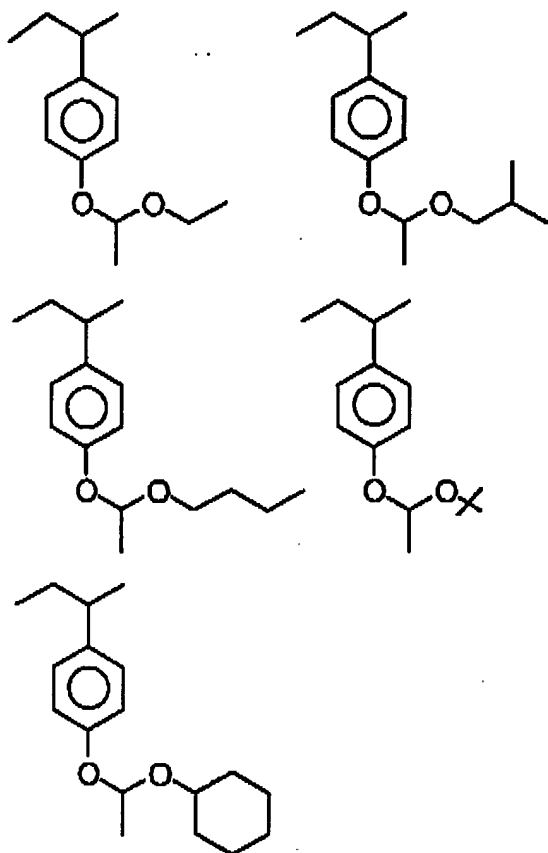
[0072]

[Ka-20]



[0073]

[Ka-21]



[0074]

Preferred examples of repeating units copolymerizable with structural units represented by general formula (VI) include structural units represented by the following general formula (VII) and general formula (VIII).

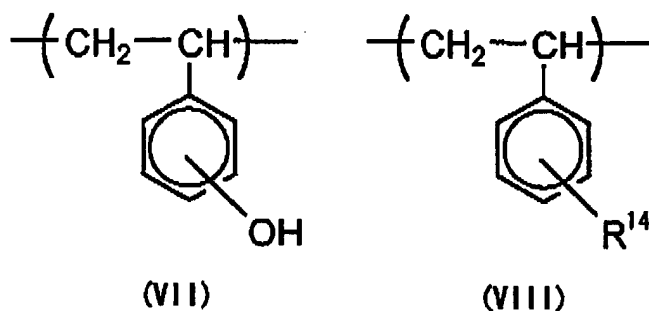
The incorporation of these structural units into the resin is effective in controlling the decomposition of the resin with an acid and the solubility thereof in an alkaline

developing solution. By the incorporation of these structural groups, a profile with excellent rectangularity can be attained.

Furthermore, the incorporation is effective in regulating the amount of structural units represented by general formula (VI).

[0075]

[Ka-22]



[0076]

R^{14} , which is a group not dissociating by the action of an acid (referred to as an acid-stable group), represents a hydrogen atom, halogen atom, alkyl group, alkoxy group, or acyloxy group.

Preferred examples of the alkyl group as the acid-stable group represented by R^{14} include alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, propyl, n-butyl, sec-butyl, and t-butyl.

[0077]

Preferred examples of the alkoxy group include alkoxy groups having 1 to 4 carbon atoms, such as methoxy, ethoxy,

hydroxyethoxy, propoxy, hydroxypropoxy, n-butoxy, isobutoxy, and sec-butoxy.

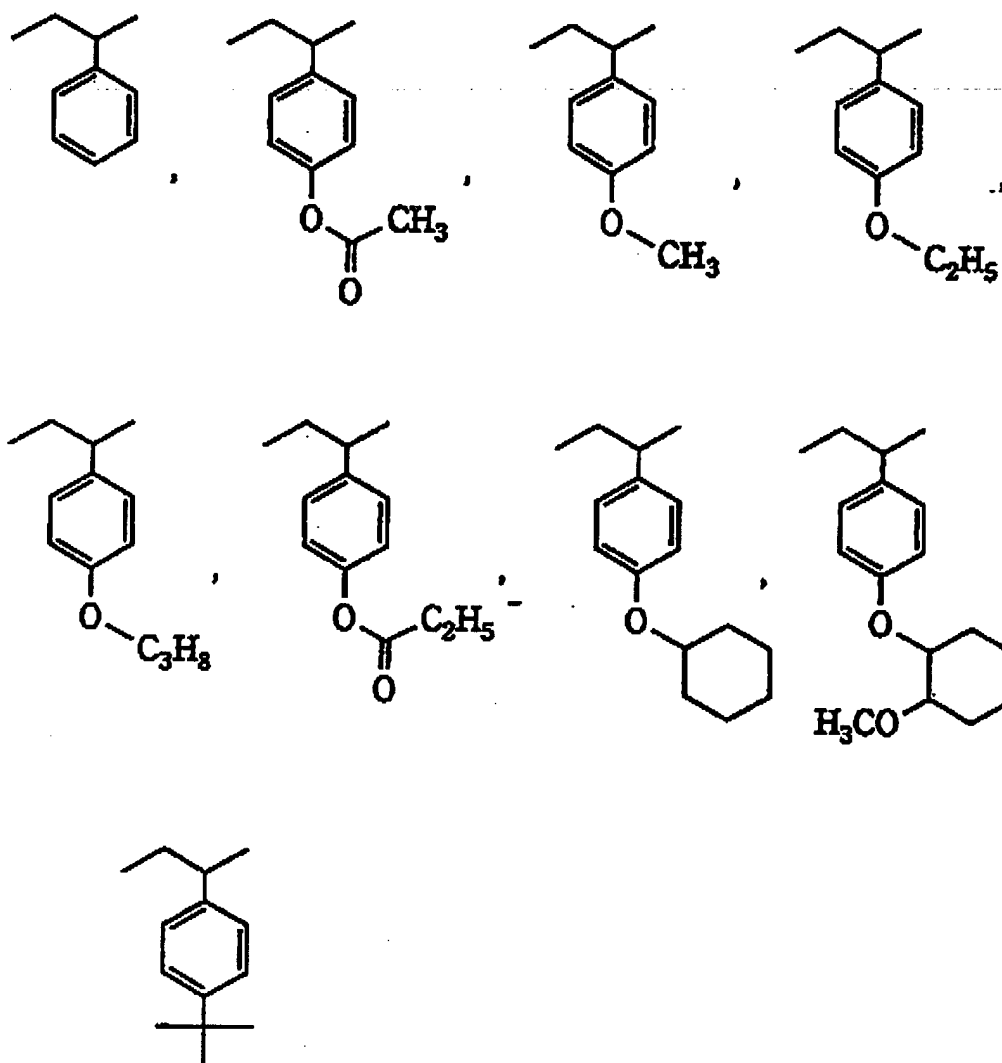
Preferred examples of the acyloxy group include ones having 2 to 7 carbon atoms, such as acetoxy, propanoyloxy, butanoyloxy, and benzoyloxy.

[0078]

Specific examples of polymerizable monomers usable for incorporating such structural units represented by general formula (VIII) include the following. However, the usable monomers should not be construed as being limited to these examples.

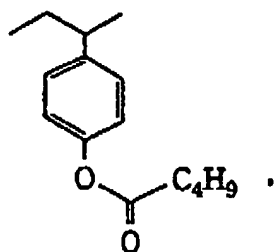
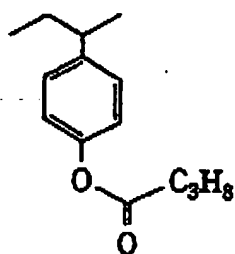
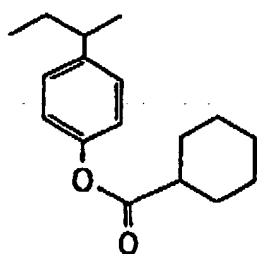
[0079]

[Ka-23]



[0080]

[Ka-24]



[0081]

The resin containing structural units represented by general formula (VII) or general formula (VIII) can be obtained, for example, by reacting a phenolic resin or a monomer thereof with an acid anhydride in the presence of a base or with the corresponding halide in the presence of a base.

[0082]

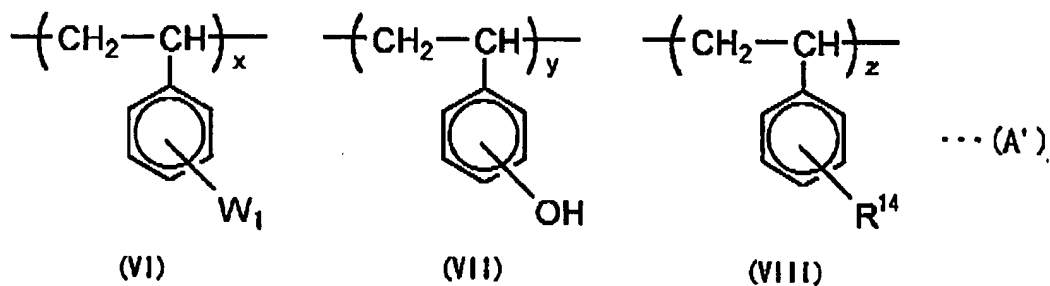
Examples of the resin according to the invention include one comprising units represented by general formula (VI) and units represented by general formula (VII), one comprising units represented by general formula (VI), units represented by general formula (VII), and units represented by general formula (VIII), and one comprising units represented by general formula (VI), units represented by general formula (VII), and t-butyl acrylate units.

[0083]

The resin according to the invention preferably is a blend containing a resin (resin (B')) comprising units represented by general formula (VI), units represented by general formula (VII), and units represented by general formula (VIII) as shown below.

[0084]

[Ka-25]



[0085]

In general formulae (VI) to (VIII), R^{14} represents the acid-stable group described above, and W_1 represents a group represented by general formula (X).

Symbols x and y each are 1 to 100 and z is 0 to 100, provided that $x+y+z=100$.

[0086]

In the resin according to the invention which is made up of units represented by general formula (VI) and units represented by general formula (VII), the proportion of the repeating units represented by general formula (VI) is generally

from 10 to 45% by mole, preferably from 15 to 40% by mole.

[0087]

In the resin made up of units represented by general formula (VI), units represented by general formula (VII), and t-butyl acrylate units, the proportion of the units represented by general formula (VI) and that of the t-butyl acrylate units are generally from 0 to 20% by mole and from 5 to 25% by mole, respectively. Preferably, the proportion of the units represented by general formula (VI) and that of the t-butyl acrylate units are from 5 to 20% by mole and from 10 to 20% by mole, respectively.

[0088]

In the resin (B') which may be contained in the resin according to the invention, the proportions x , y , and z preferably satisfy the following requirements.

[0089]

When $z=0$,

$$0.05 < x/(x+y) < 0.50$$

more preferably $0.1 < x/(x+y) < 0.45$.

When $z>0$,

$$(1) \quad 0.05 < x/(x+y+z) < 0.35,$$

$$(2) \quad 0.005 < z/(x+y+z) < 0.25,$$

$$(3) \quad x \geq z, \text{ and}$$

$$(4) \quad 0.5 < x/(x+z) < 0.95,$$

more preferably

$$(1) \ 0.1 < x/(x+y+z) < 0.25,$$

$$(2) \ 0.01 < z/(x+y+z) < 0.15,$$

$$(3) \ x \geq z, \text{ and}$$

$$(4) \ 0.5 < x/(x+y) < 0.85.$$

[0090]

When the resin according to the invention satisfies those requirements, profile rectangularity is improved and, in particular, development defects are further diminished.

[0091]

The repeating structural units represented by general formula (VI), general formula (VII), or general formula (VIII) present in the resin or the repeating structural units derived from any other polymerizable monomer which may be present in the resin each may be of one kind or comprise a combination of two or more kinds.

The resin to be contained in the positive photoresist composition of the invention may be one in which one or more other appropriate monomers have been copolymerized so as to incorporate alkali-soluble groups, e.g., phenolic hydroxyl groups or carboxyl groups, and to thereby enable the resin to retain satisfactory developability with an alkaline developing solution.

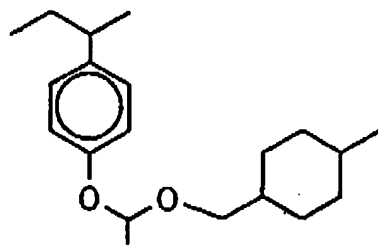
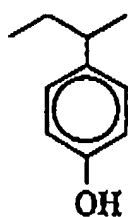
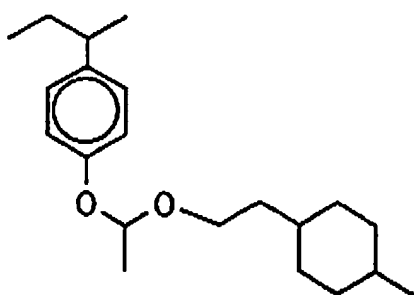
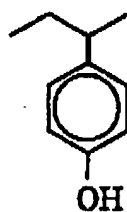
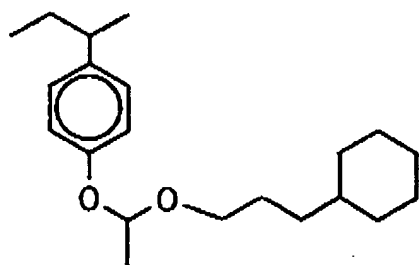
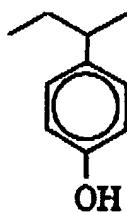
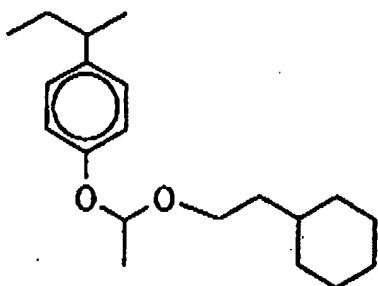
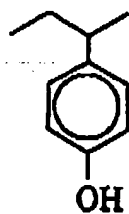
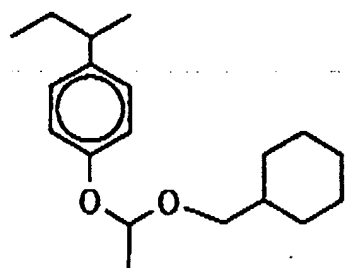
[0092]

Examples of such structures in the resin according to the invention are shown below, but the resin to be used in

the invention should not be construed as being limited to ones comprising these units.

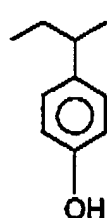
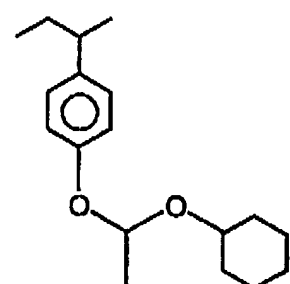
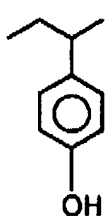
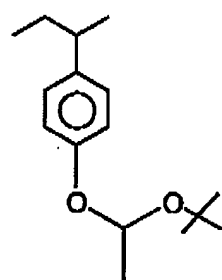
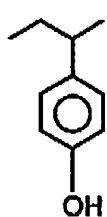
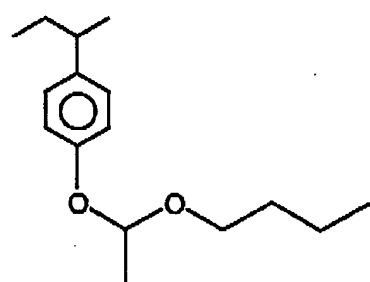
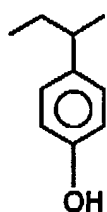
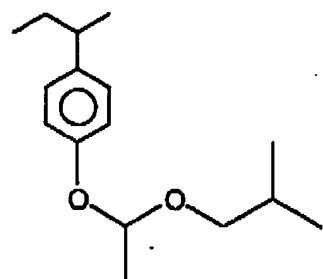
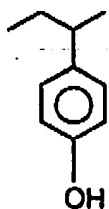
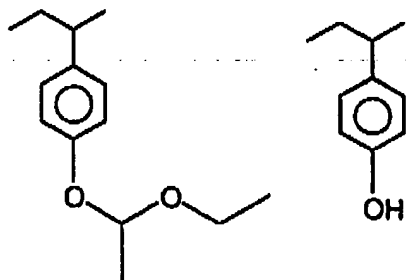
[0093]

[Ka-26]



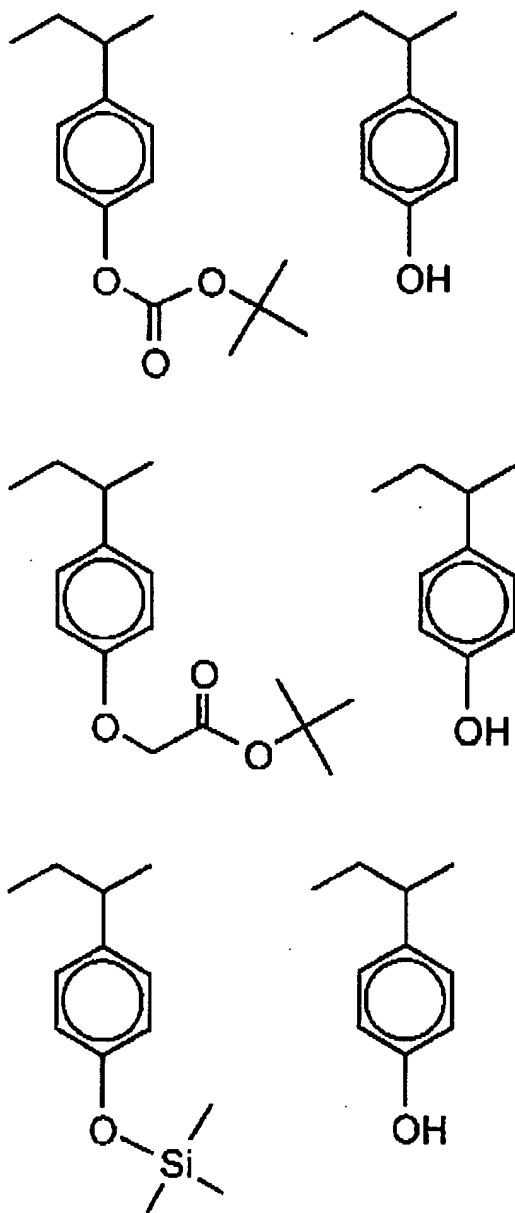
[0094]

[Ka-27]



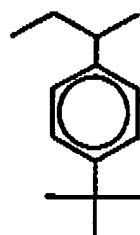
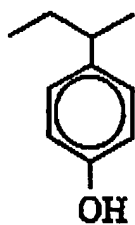
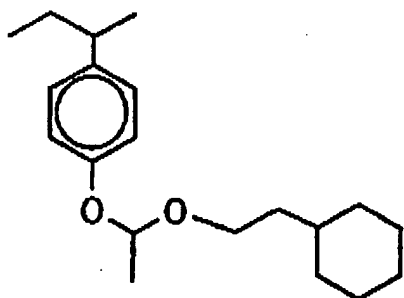
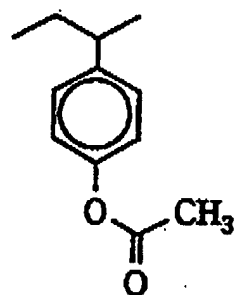
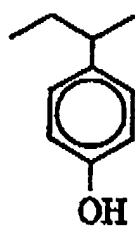
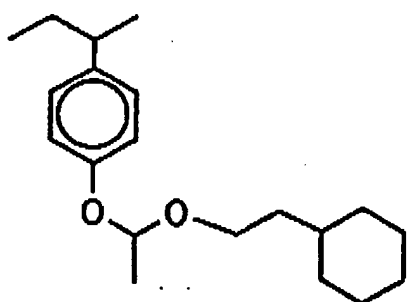
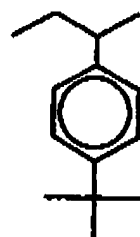
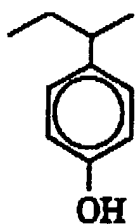
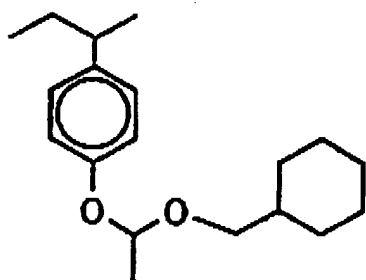
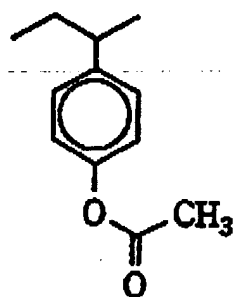
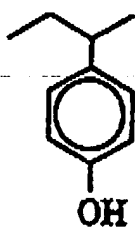
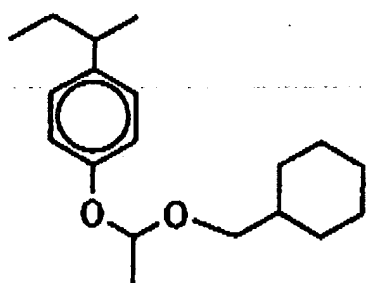
[0095]

[Ka-28]



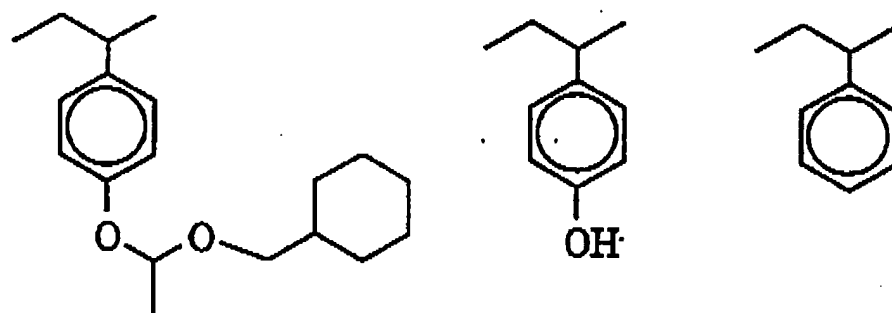
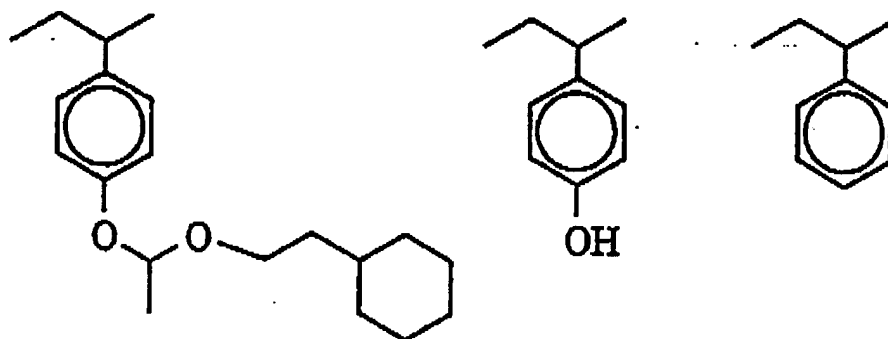
[0096]

[Ka-29]



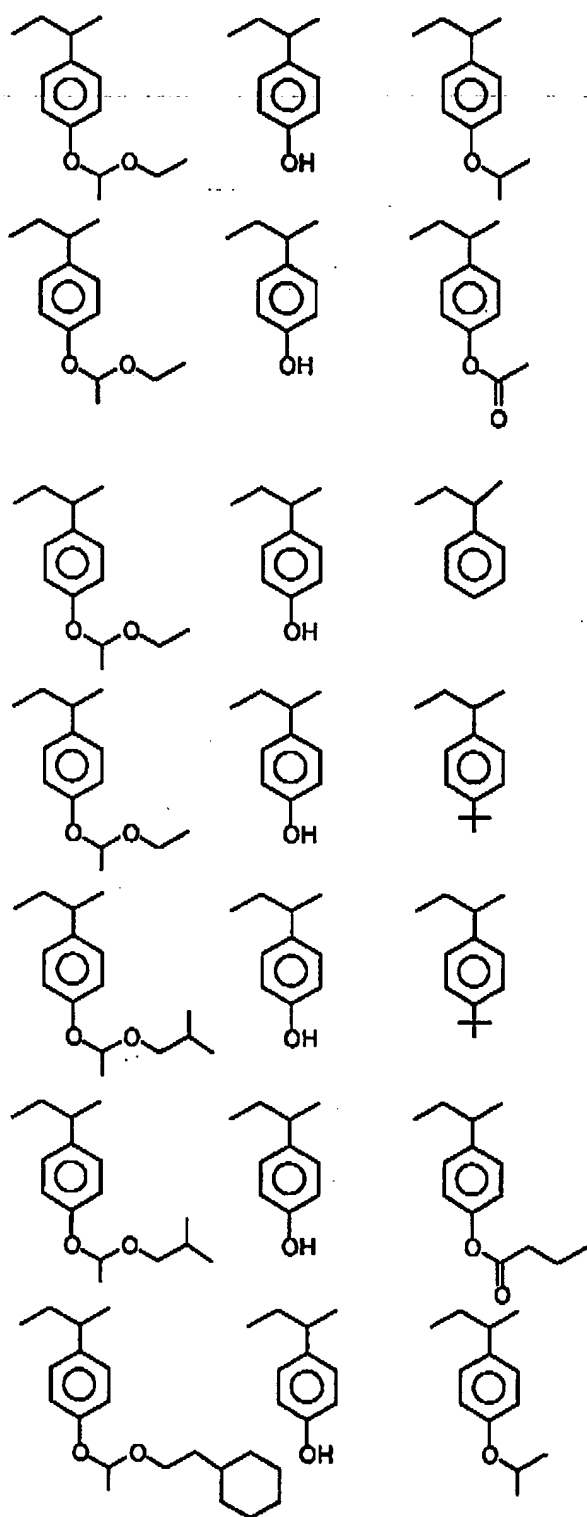
[0097]

[Ka-30]



[0098]

[Ka-31]



[0099]

The molecular weight of the resin described above is generally 2,000 or higher, preferably from 3,000 to 200,000, more preferably from 5,000 to 70,000, in terms of weight-average molecular weight (M_w ; calculated for standard polystyrene).

The dispersity ratio (M_w/M_n) thereof is preferably from 1.0 to 4.0, more preferably from 1.0 to 3.5, especially preferably from 1.0 to 3.0. The smaller the dispersity ratio, the better the heat resistance and image-forming properties (pattern profile, defocus latitude, etc.).

[0100]

The content of the resin described above in the positive photoresist composition (excluding the solvent for application) is preferably from 50 to 99% by weight, more preferably from 75 to 98% by weight.

[0101]

[4] Fluororesin-Group-Containing Polymeric Compound (C)

The fluoroaliphatic-group-containing polymeric compound (C) to be used in the invention is a polymer having repeating units derived from a monomer represented by general formula (2) described above (hereinafter referred to also as fluoropolymer).

Although the fluoropolymer to be used in the invention is not particularly limited as long as it satisfies that requirement, useful fluoropolymers are acrylic resins,

methacrylic resins, and copolymers thereof with one or more vinyl monomers copolymerizable therewith.

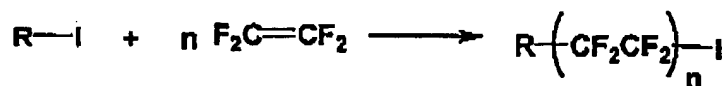
[0102]

One kind of the fluoroaliphatic groups in the fluoropolymer according to the invention are derived from a fluoroaliphatic compound produced by the telomerization method (also called the telomer method) or by the oligomerization method (also called the oligomer method). These processes for producing a fluoroaliphatic compound are described, for example, in *Fusso Kagôbutsu No Gôsei To Kinô* (supervised by Nobuo Ishikawa, published by CMC Publishing Co., Ltd., 1987) pp.117-118 and *Chemistry of Organic Fluorine Compounds II* (Monograph 187, ed. by Milos Hudlicky and Attila E. Pavlath, American Chemical Society, 1995) pp.747-752. The telomerization method is a process in which an alkyl halide having a large chain transfer constant, e.g., an iodide, is used as a telogen to conduct radical polymerization of a fluorine-containing vinyl compound, e.g., tetrafluoroethylene, to synthesize a telomer (an example is shown by Scheme 1).

[0103]

[Ka-32]

Scheme1



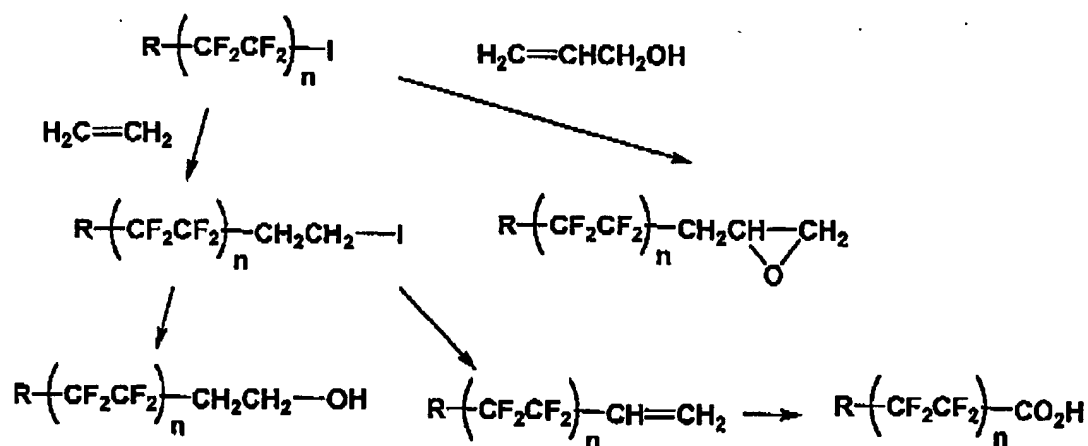
[0104]

The iodine-terminated telomer obtained is usually subjected to an appropriate terminal chemical modification, such as those shown by Scheme 2, and thereby converted to fluoroaliphatic compounds. These compounds are further converted, according to need, into desired monomer structures before being used in producing a fluoroaliphatic-group-containing polymer.

[0105]

[Ka-33]

Scheme2



[0106]

In general formula (2) in the invention, R_6 represents a hydrogen atom or methyl group, and X represents an oxygen atom, sulfur atom, or $-N(R_7)-$, wherein R_7 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, i.e., methyl, ethyl, propyl, or butyl. Preferably, R_7 is a hydrogen atom or methyl. X preferably is an oxygen atom.

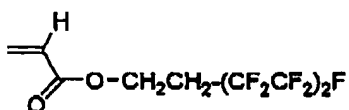
Symbol p in general formula (2) is preferably an integer of 1 to 6, especially preferably 2.

Symbol q in general formula (2) is 2 to 4. A mixture of monomers represented by general formula (2) in which q is two or more of 2 to 4 may be used.

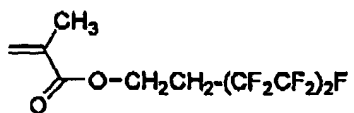
Specific examples of the fluoroaliphatic-group-containing monomer represented by general formula (2) are shown below, but the monomer should not be construed as being limited to these examples.

[0107]

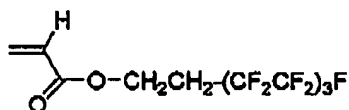
[Ka-34]



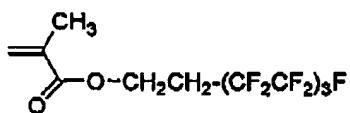
F-1



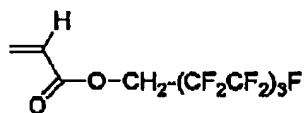
F-2



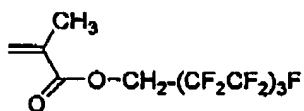
F-3



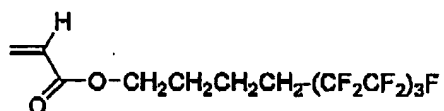
F-4



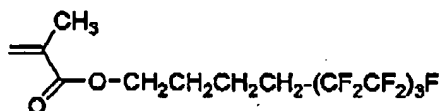
F-5



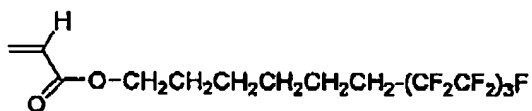
F-6



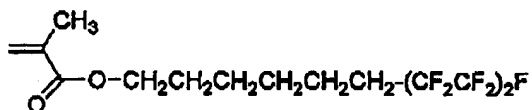
F-7



F-8



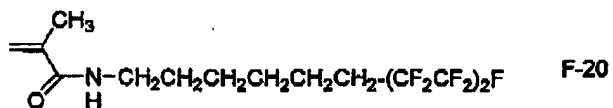
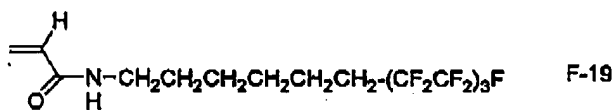
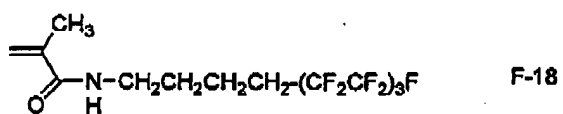
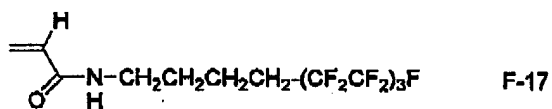
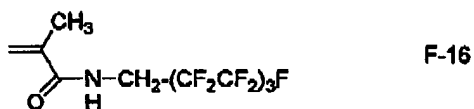
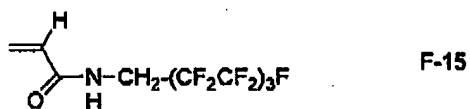
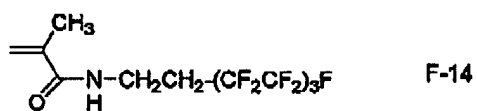
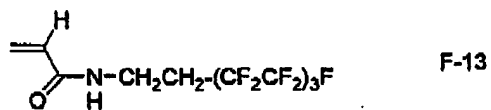
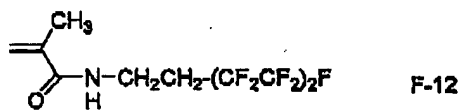
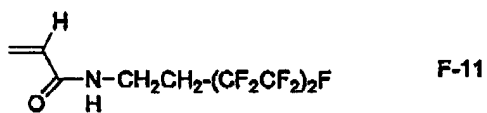
F-9



F-10

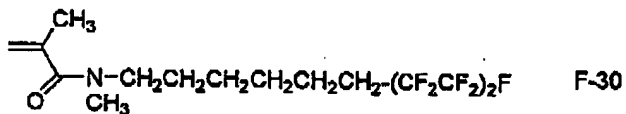
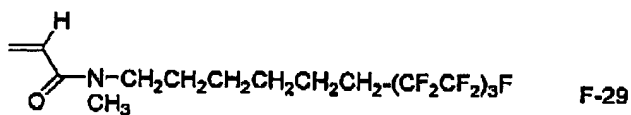
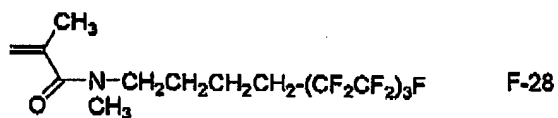
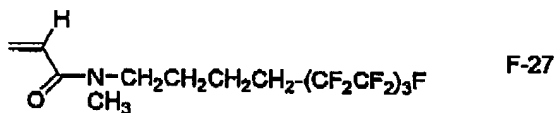
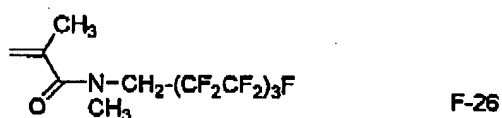
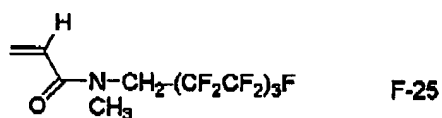
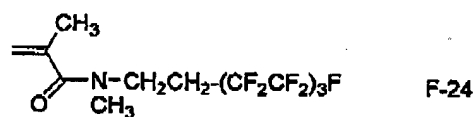
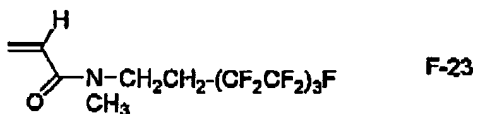
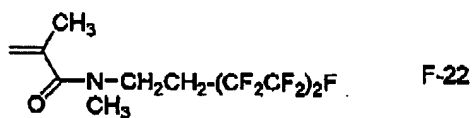
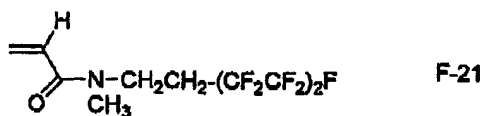
[0108]

[Ka-35]



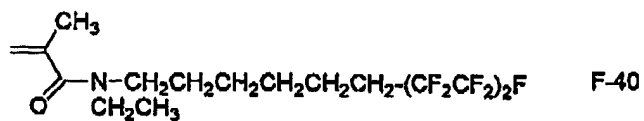
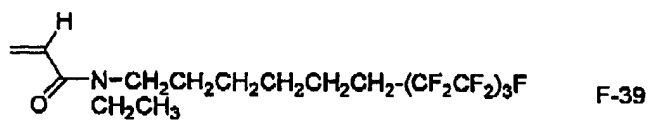
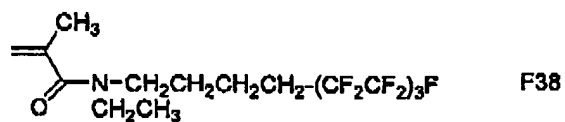
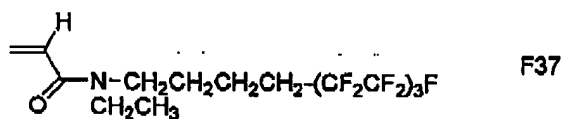
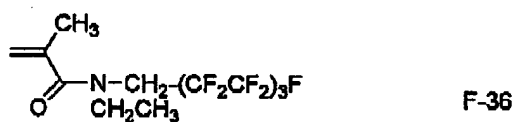
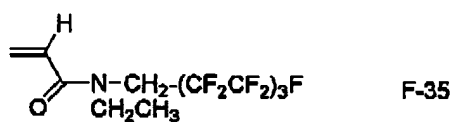
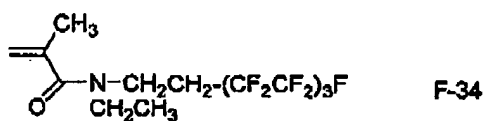
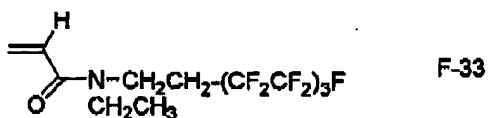
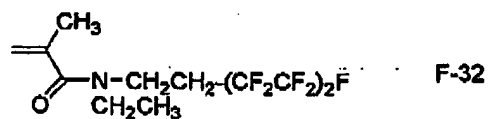
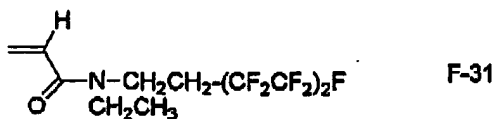
[0109]

[Ka-36]



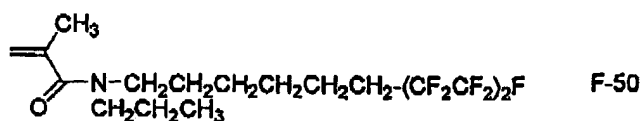
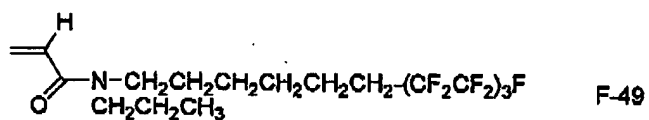
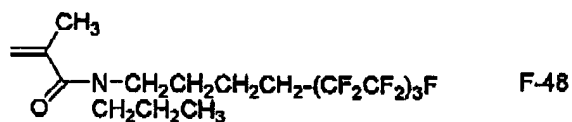
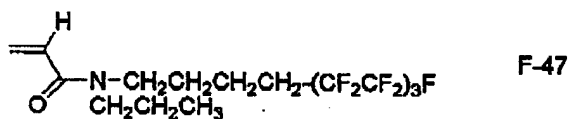
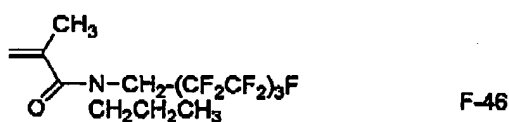
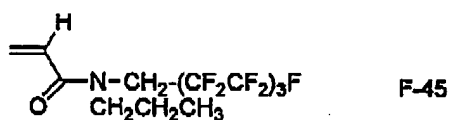
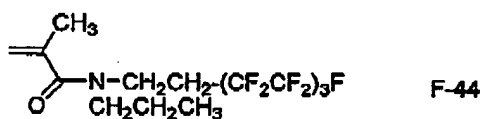
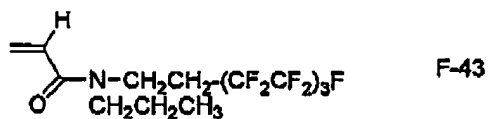
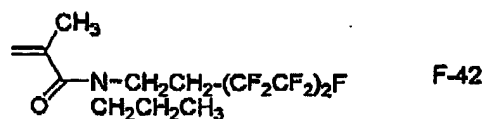
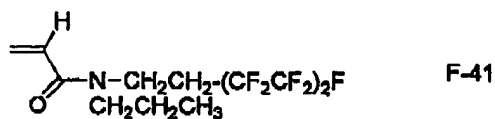
[0110]

[Ka-37]



[0111]

[Ka-38]

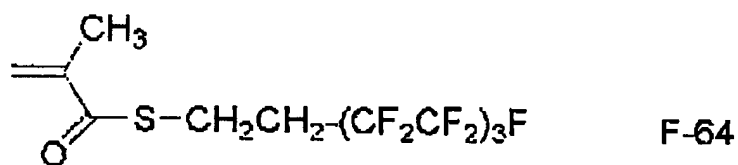
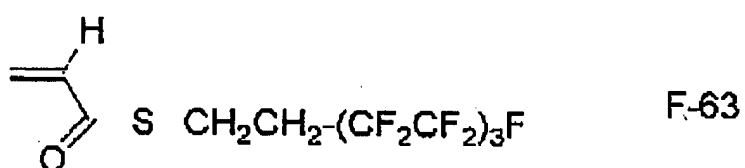
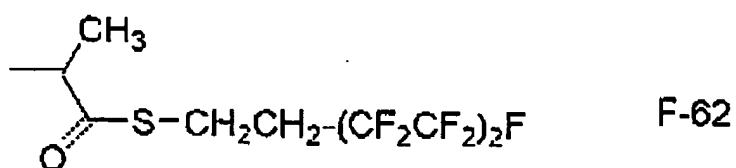
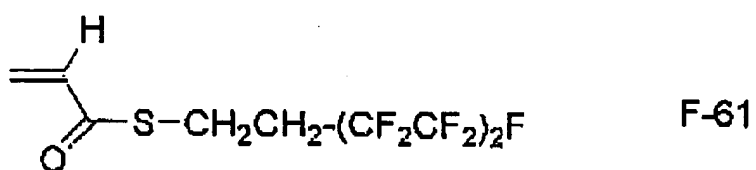


[0112]

[Ka-39]

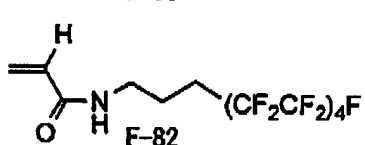
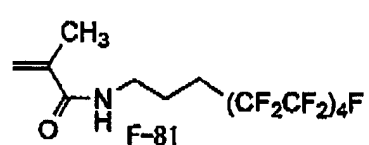
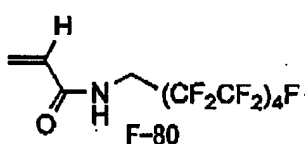
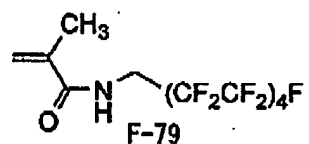
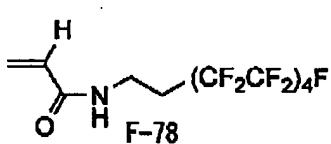
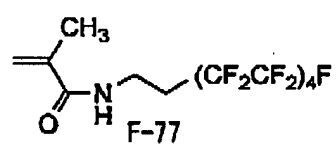
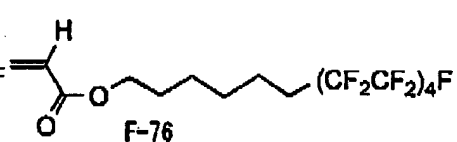
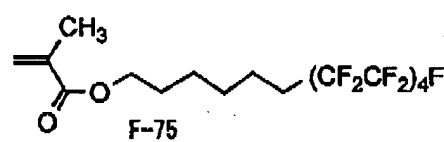
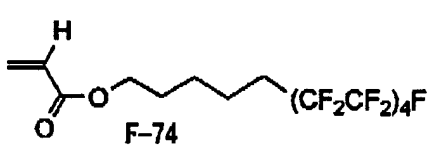
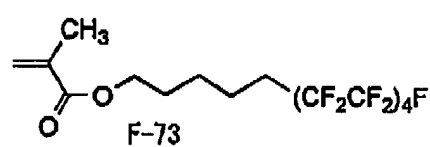
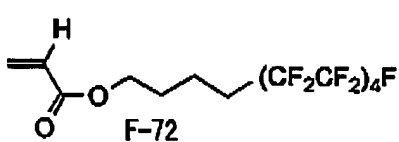
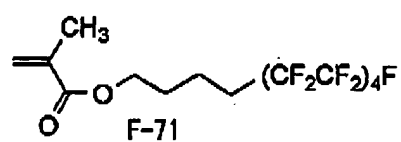
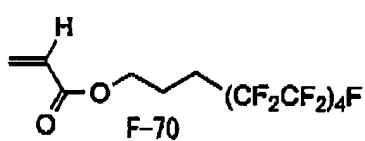
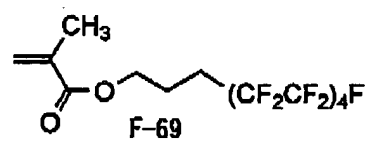
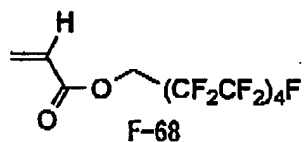
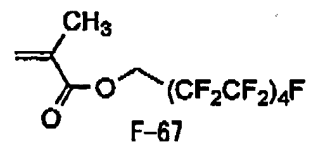
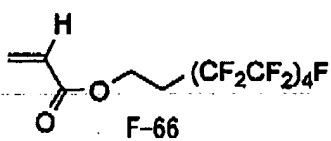
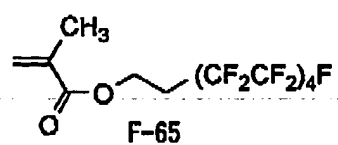
[0113]

[Ka-40]



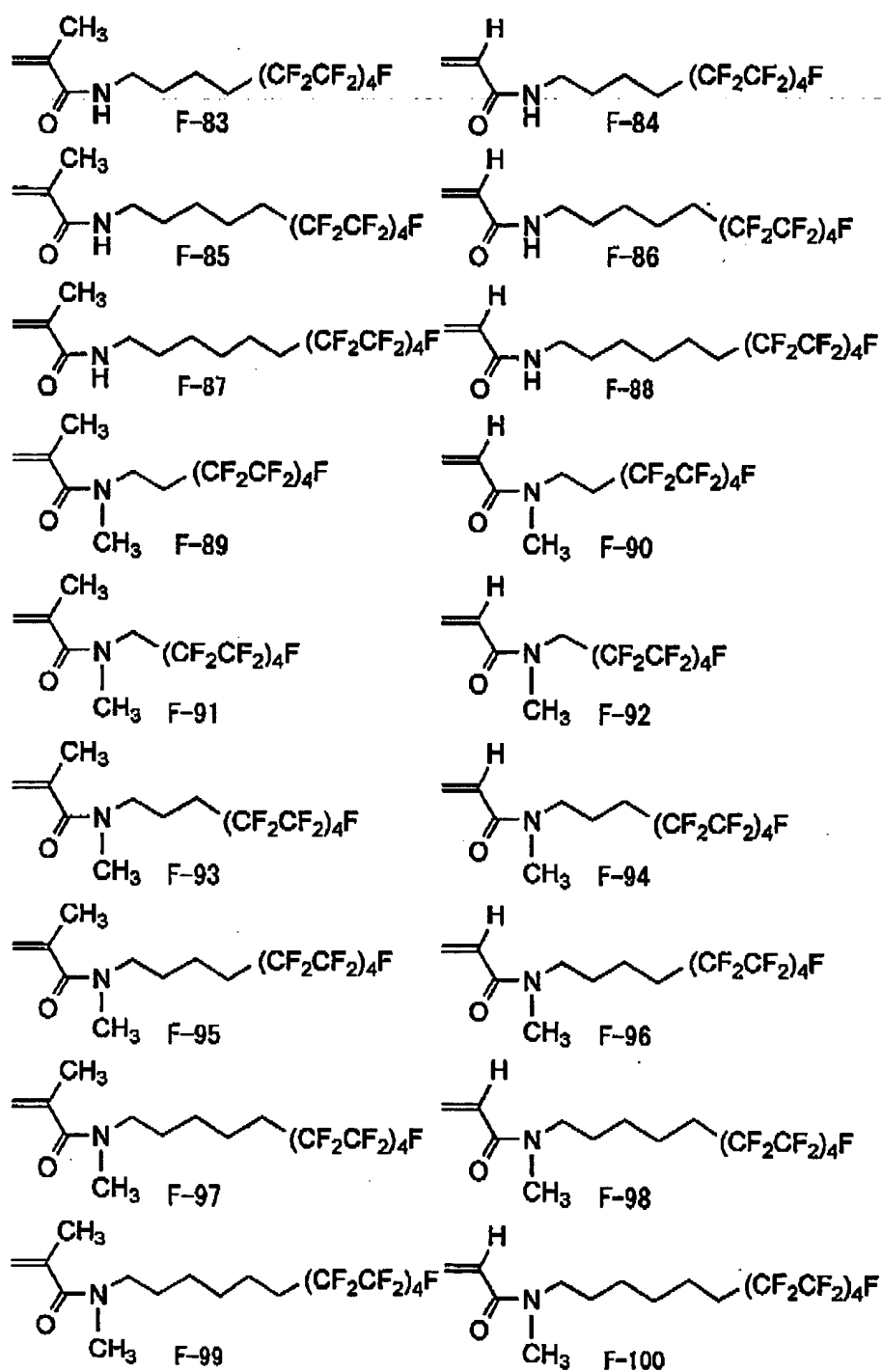
[0114]

[Ka-41]



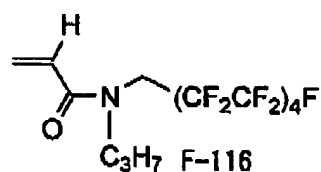
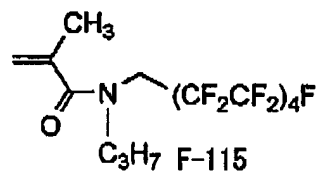
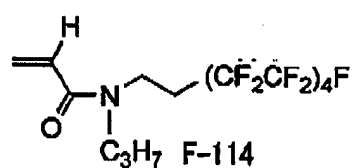
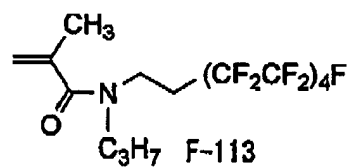
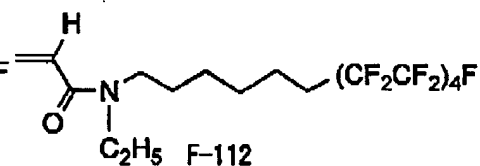
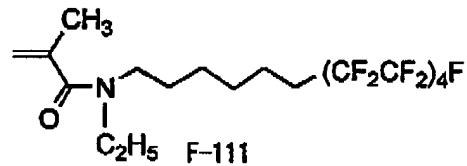
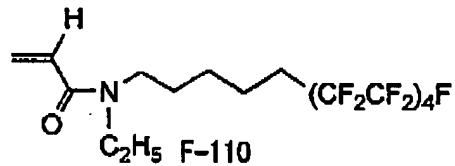
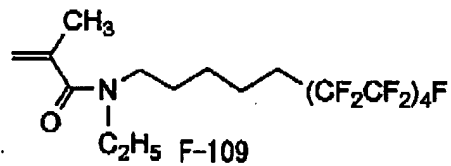
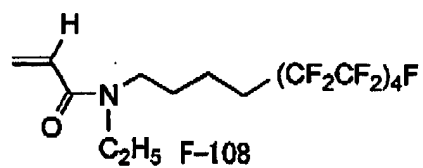
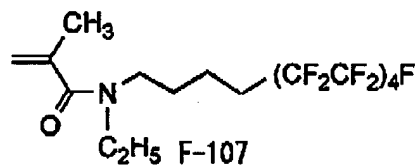
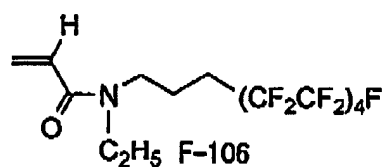
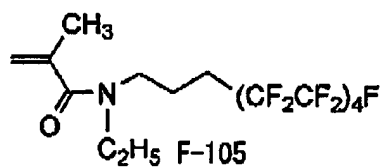
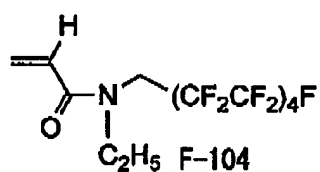
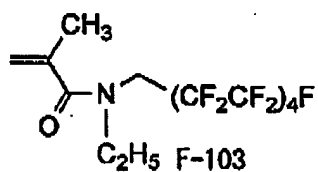
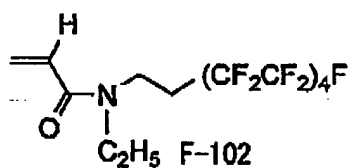
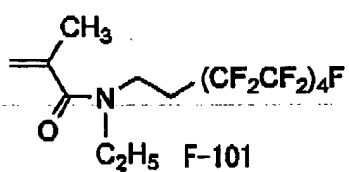
[0115]

[Ka-42]



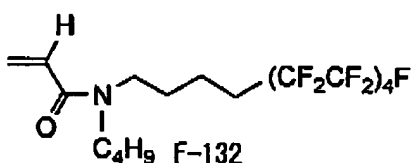
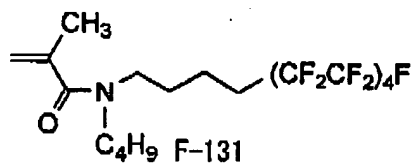
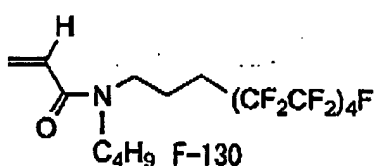
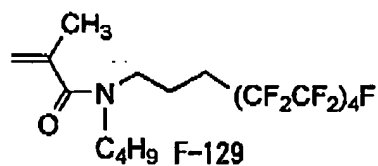
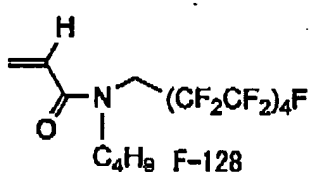
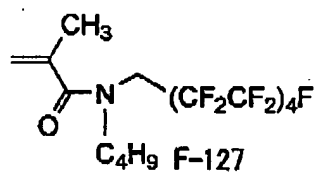
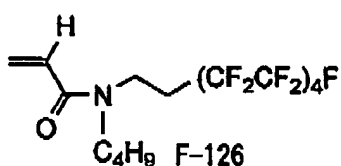
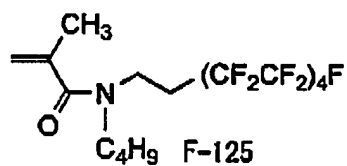
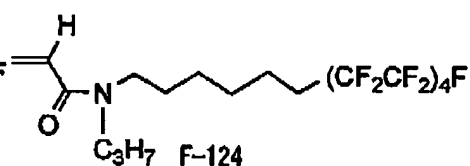
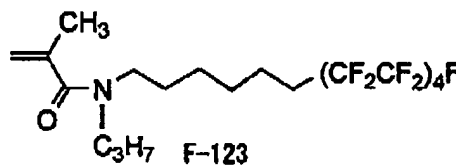
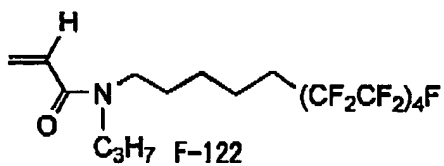
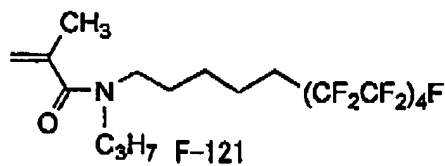
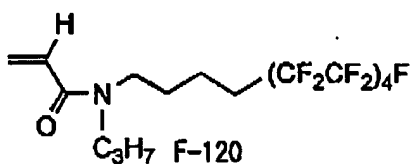
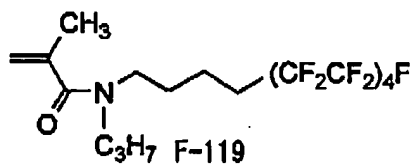
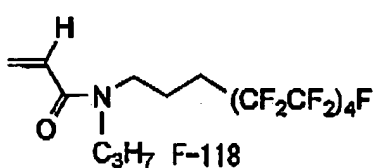
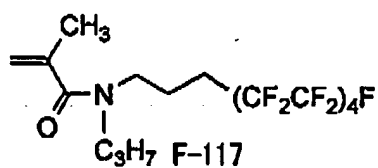
[0116]

[Ka-43]



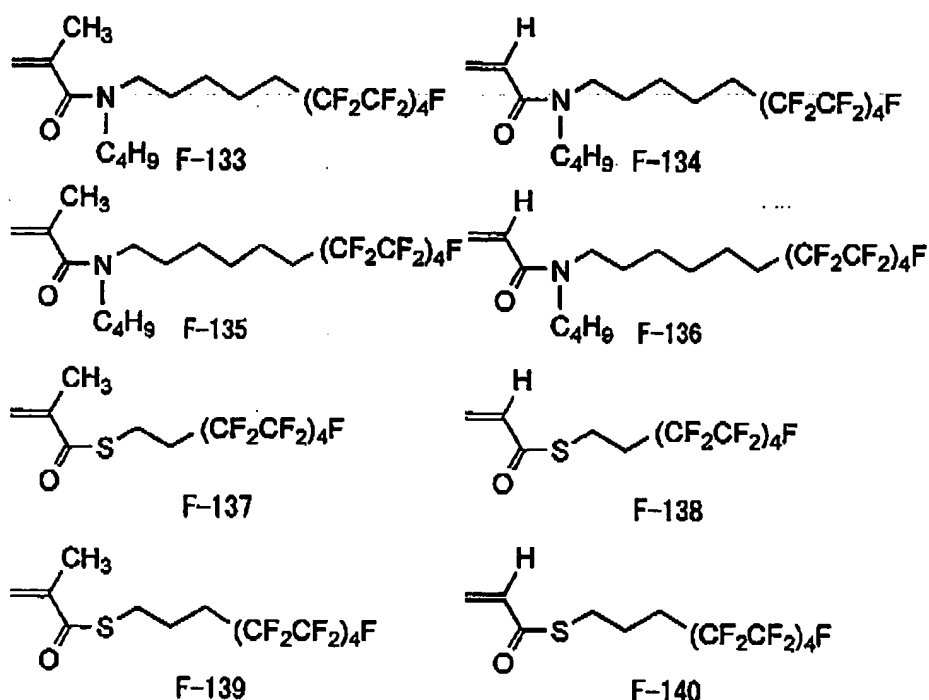
[0117]

[Ka-44]



[0118]

[Ka-45]



[0119]

The fluoropolymer preferably is a copolymer of one or more monomers represented by formula (2) with a poly(oxyalkylene) acrylate and/or a poly(oxyalkylene) methacrylate.

The poly(oxyalkylene) group can be represented by $(\text{OR})_x$. R preferably is an alkylene group having 2 to 4 carbon atoms, e.g., $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}_2-$, or $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$.

The oxyalkylene units in the poly(oxyalkylene) group may be the same unit like those in poly(oxypropylene), or may be two or more different kinds of oxyalkylene units irregularly distributed. The oxyalkylene units may also be oxypropylene or oxyethylene units arranged linearly or branch-wise.

Furthermore, the group may comprise a linear or branched block

made up of oxypropylene units and a linear or branched block made up of oxyethylene units.

This poly(oxyalkylene) chain can include one composed of such poly(oxyalkylene) chains connected to each other by one or more chain-connecting bonds (e.g., -CONH-Ph-NHCO- or -S-; Ph represents a phenylene group). When such chain-connecting bonds include one having a valence of 3 or higher, this provides means for obtaining a branched oxyalkylene unit chain. In the case where this copolymer is to be used in the invention, an appropriate range of the molecular weight of the poly(oxyalkylene) group is from 250 to 3,000.

A poly(oxyalkylene) acrylate or methacrylate can be produced by reacting a commercial hydroxy poly(oxyalkylene) material, e.g., one solid under the trade name of "Pluronic" (manufactured by Asahi Denka Kogyo K.K.), "Adeka Polyether" (manufactured by Asahi Denka Kogyo K.K.), "Carbowax" (manufactured by Glico Products), "Toriton" (manufactured by Rohm and Hass), and P.E.G. (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), with acrylic acid, methacrylic acid, acryloyl chloride, methacryloyl chloride, acrylic anhydride, or the like by a known method. Alternatively, a poly(oxyalkylene) diacrylate or the like produced by a known method can be used.

[0120]

A preferred poly(oxyalkylene) (meth)acrylate for use as an ingredient to be copolymerized is poly(oxyethylene)

(meth)acrylate, because use of this ingredient improves solubility in developing solutions.

In an especially preferred embodiment, the fluoropolymer is a polymer obtained by copolymerizing three or more monomers, i.e., at least one monomer represented by general formula (2), poly(oxyethylene) (meth)acrylate, and at least one poly(oxyalkylene) (meth)acrylate. This poly(oxyalkylene) (meth)acrylate is a monomer different from poly(oxyethylene) (meth)acrylate.

More preferably, the fluoropolymer is a terpolymer formed from poly(oxyethylene) (meth)acrylate, poly(oxypropylene) (meth)acrylate, and a monomer represented by general formula (2).

The proportion of the poly(oxyethylene) (meth)acrylate to be copolymerized is preferably from 0.5 to 20% by mole, more preferably from 1 to 10% by mole, based on all monomers.

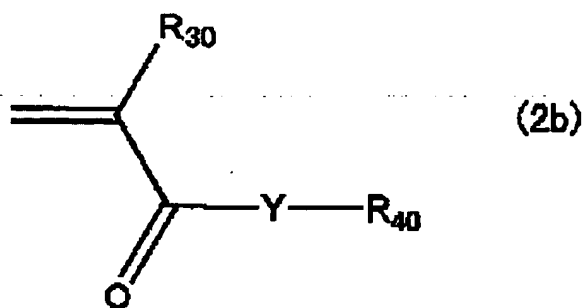
[0121]

The fluoropolymer preferably further contains comonomer units derived from a monomer represented by the following general formula (2b).

General Formula (2b)

[0122]

[Ka-46]



[0123]

(In general formula (2b), R_{30} represents a hydrogen atom or a methyl group, Y represents a bivalent connecting group, and R_{40} represents a linear, branched, or cyclic alkyl group which has 4 to 20 carbon atoms and may have one or more substituents.)

[0124]

In general formula (2b), R_{30} represents a hydrogen atom or methyl group, and Y represents a bivalent connecting group.

The bivalent connecting group preferably is an oxygen atom, sulfur atom, $-N(R_{50})-$, or the like, wherein R_{50} preferably is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, or butyl. More preferably, R_{50} is a hydrogen atom or methyl.

Y more preferably is an oxygen atom, $-N(H)-$, or $-N(CH_3)-$.

R_{40} represents a linear, branched, or cyclic alkyl group which has 4 to 20 carbon atoms and may have one or more substituents.

Examples of the substituents of the alkyl group represented by R_{40} include hydroxyl, alkylcarboxyl groups, arylcarbonyl groups, carboxyl, alkyl ether groups, aryl ether groups, halogen atoms such as fluorine, chlorine, and bromine, nitro, cyano,

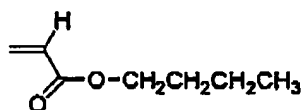
and amino. However, the substituents should not be construed as being limited to these examples. Preferred examples of the linear, branched, or cyclic alkyl group having 4 to 20 carbon atoms include linear or branched alkyl groups such as butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, octadecyl, and eicosanyl, monocyclic alkyl groups such as cyclohexyl and cycloheptyl, and polycyclic alkyl groups such as bicycloheptyl, bicyclododecyl, tricycloundecyl, tetracyclododecyl, adamantyl, norbornyl, and tetracyclododecyl.

[0125]

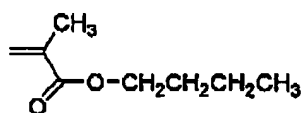
Specific examples of the monomer represented by general formula (2b) include the following monomers, but these examples should not be construed as limiting the monomer of general formula (2b).

[0126]

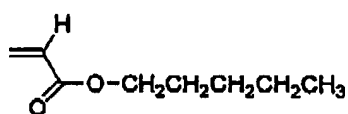
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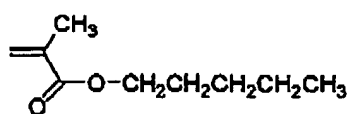
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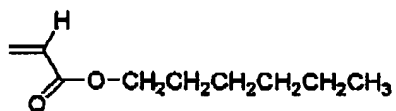
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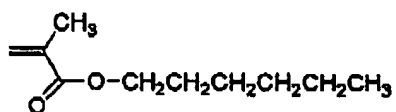
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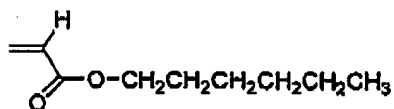
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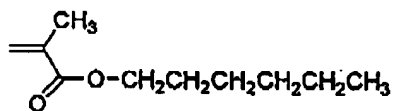
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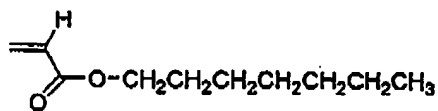
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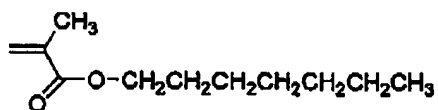
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A-8



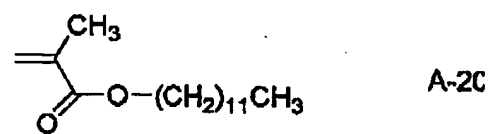
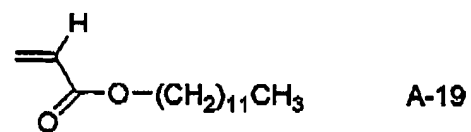
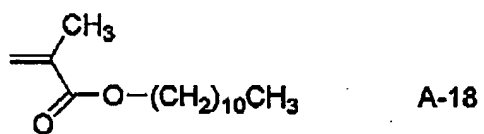
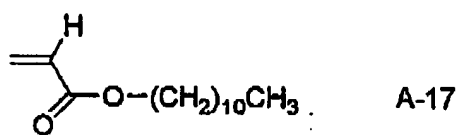
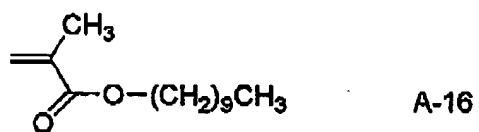
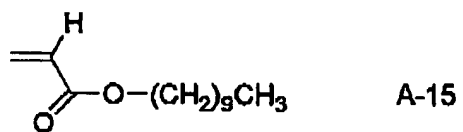
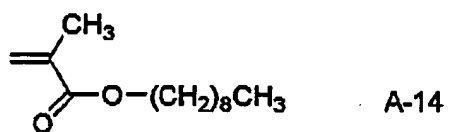
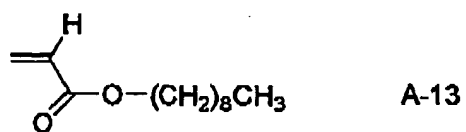
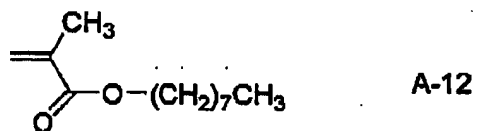
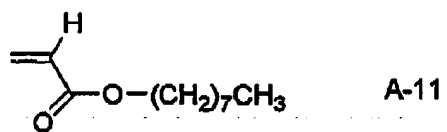
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A-10

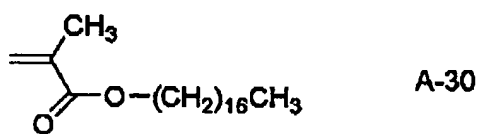
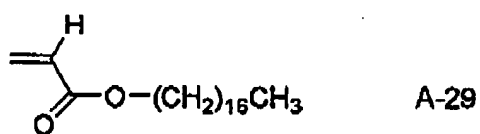
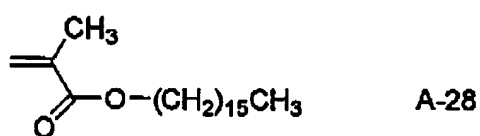
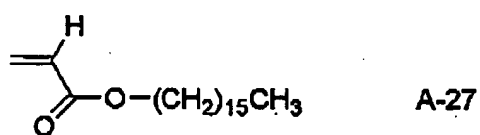
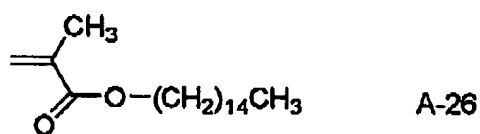
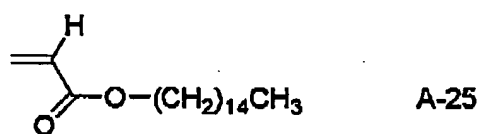
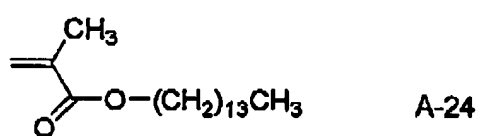
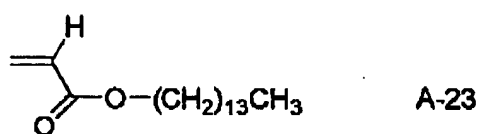
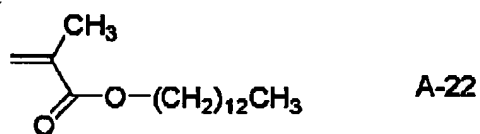
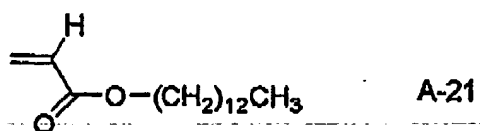
[0127]

[Ka-48]



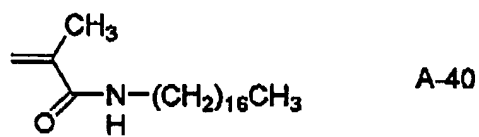
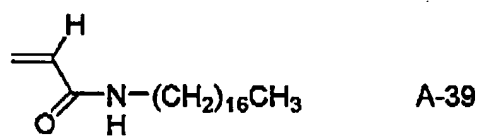
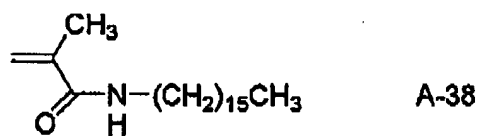
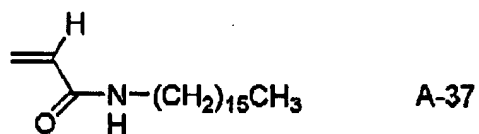
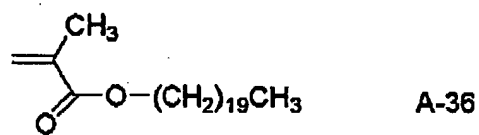
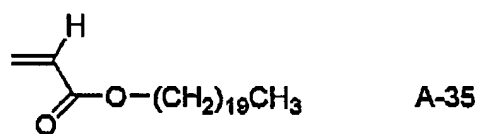
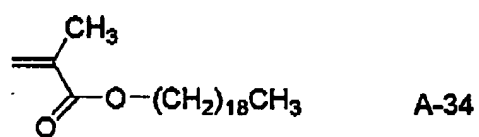
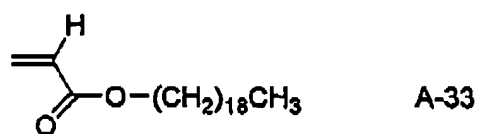
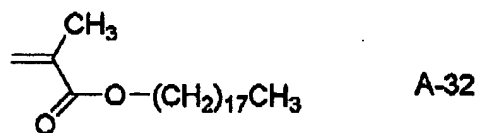
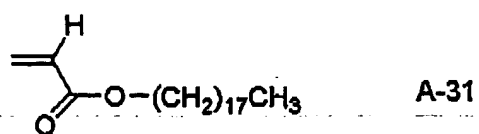
[0128]

[Ka-49]



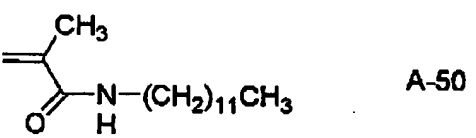
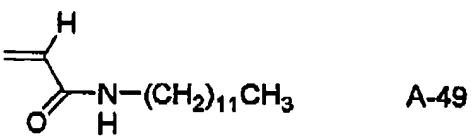
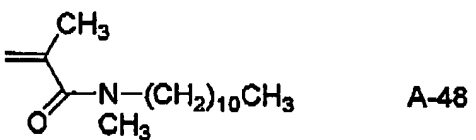
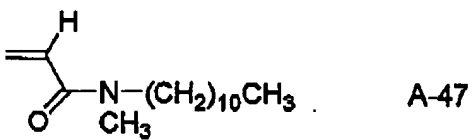
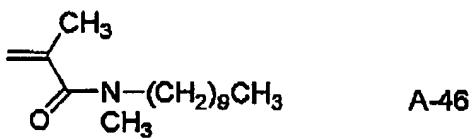
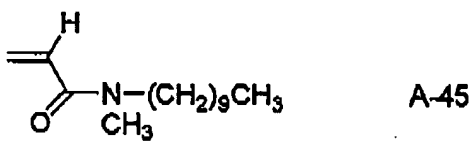
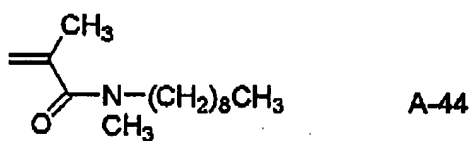
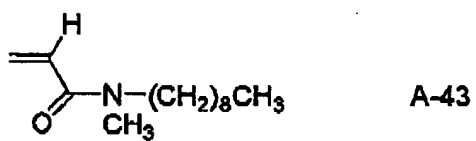
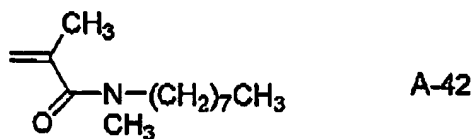
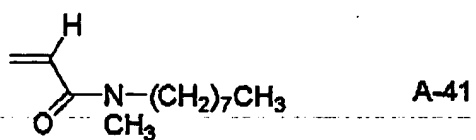
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[Ka-50]



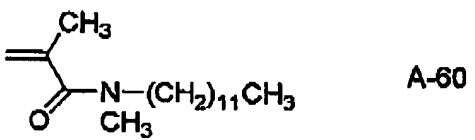
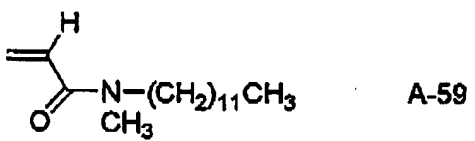
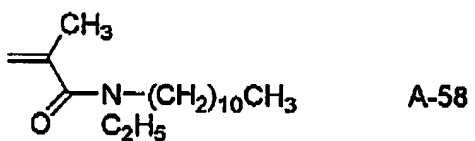
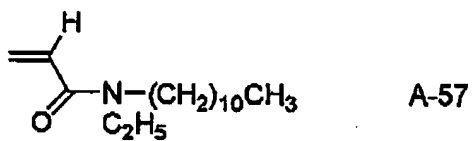
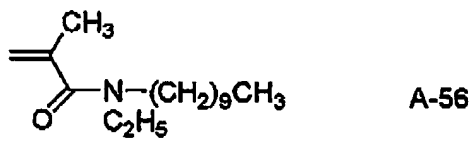
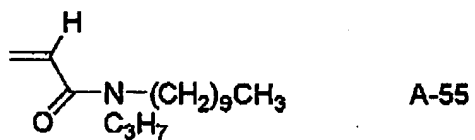
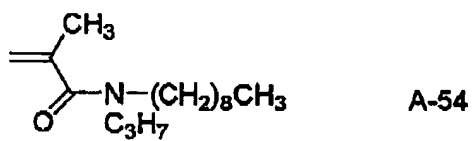
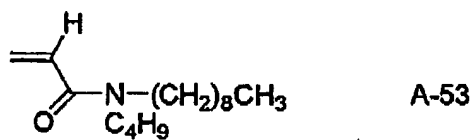
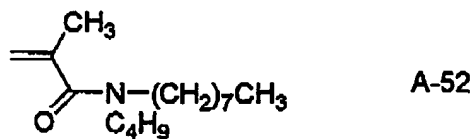
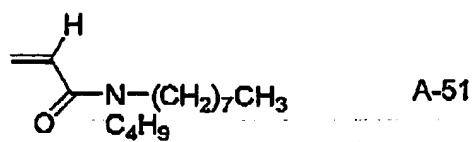
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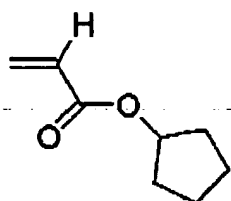
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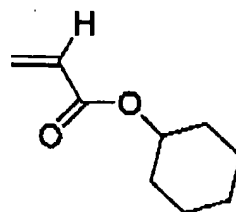


[0132]

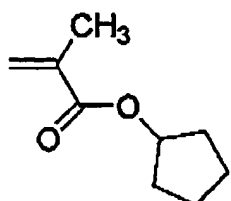
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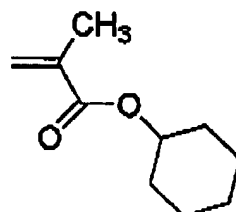
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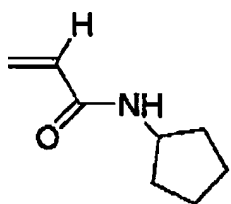
A-67



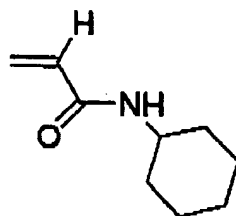
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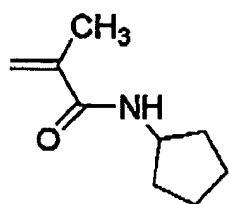
A-68



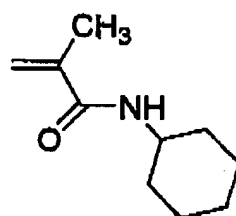
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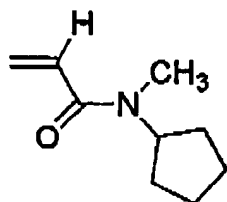
A-69



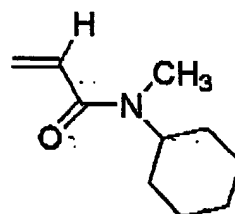
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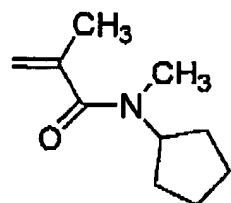
A-70



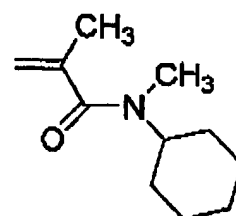
A-65



A-71



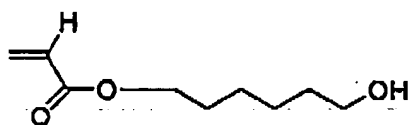
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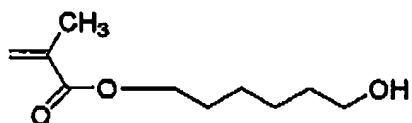
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[0133]

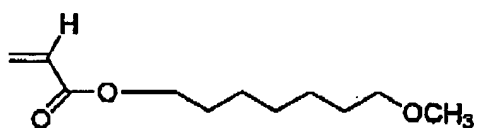
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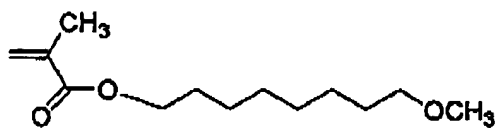
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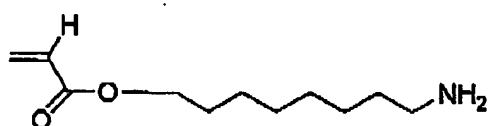
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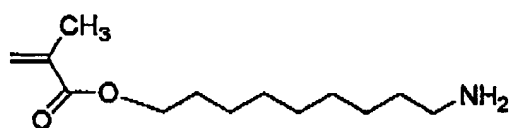
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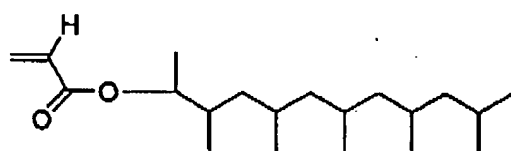
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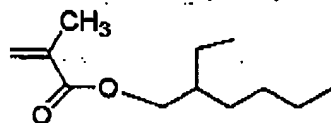
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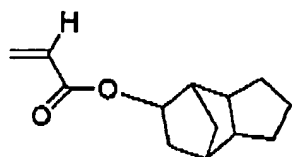
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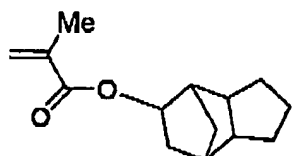
A-79



A-80



A-81



A-82

[0134]

Besides a poly(oxyalkylene) acrylate and/or a poly(oxyalkylene) methacrylate, which are preferred ingredients, and besides the monomer represented by general formula (2b), monomers copolymerizable with these can be reacted.

The proportion of these copolymerizable monomers to be copolymerized may be up to 20% by mole, preferably up to 10% by mole, based on all monomers.

As these monomers can be used ones described in *Polymer Handbook*, 2nd, ed., J. Brandrup, Wiley Interscience (1975), Chapter 2, pp. 1-483.

Examples thereof include compounds having one addition-polymerizable unsaturated bond, such as acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, acrylamide and derivatives thereof, methacrylamide and derivatives thereof, allyl compounds, vinyl ethers, and vinyl esters.

[0135]

Specific examples of those monomers include the following.

Acrylic Esters:

Methyl acrylate, ethyl acrylate, propyl acrylate, chloroethyl acrylate, 2-hydroxyethyl acrylate, trimethylolpropane monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, and

tetrahydrofurfuryl acrylate.

Methacrylic Esters:

Methyl methacrylate, ethyl methacrylate, propyl methacrylate, chloroethyl methacrylate, 2-hydroxyethyl methacrylate, trimethylolpropane monomethacrylate, benzyl methacrylate, methoxybenzyl methacrylate, furfuryl methacrylate, and tetrahydrofurfuryl methacrylate.

[0136]

Acrylamide and Derivatives:

Acrylamide, N-alkylacrylamides (the alkyl is one having 1 to 3 carbon atoms, e.g., methyl, ethyl, or propyl), N,N-dialkylacrylamides (the alkyls each are one having 1 to 3 carbon atoms), N-hydroxyethyl-N-methylacrylamide, and N-2-acetamidoethyl-N-acetylacrylamide.

Methacrylamide and Derivatives:

Methacrylamide, N-alkylmethacrylamides (the alkyl is one having 1 to 3 carbon atoms, e.g., methyl, ethyl, or propyl), N,N-dialkylmethacrylamides (the alkyls each are one having 1 to 3 carbon atoms), N-hydroxyethyl-N-methylmethacrylamide, and N-2-acetamidoethyl-N-acetylmethacrylamide.

Allyl Compounds:

Allyl esters (e.g., allyl acetate, allyl caproate, allyl caprate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, and allyl lactate) and allyloxyethanol.

[0137]

Vinyl Ethers:

Alkyl vinyl ethers (e.g., hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, and butylaminoethyl vinyl ether, benzyl vinyl ether, and tetrahydrofurfuryl vinyl ether.

Vinyl Esters:

Vinyl bityrate, vinyl isobutyrate, vinyl trimethylacetate, vinyl diethylacetate, vinyl valerate, vinyl caproate, vinyl chloroacetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl lactate, vinyl β -phenylbutyrate, and vinyl cyclohexylcarboxylate.

[0138]

Dialkyl Itaconates:

Dimethyl itaconate, diethyl itaconate, and dibutyl itaconate.

Dialkyl Esters or Monoalkyl Esters of Fumaric Acid:

Dibutyl fumarate.

Other monomers such as crotonic acid, itaconic acid, acrylonitrile, methacrylonitrile, maleonitrile, and styrene.

[0139]

Incidentally, part of the fluorochemicals produced by the electrolytic fluorination process, which have been frequently used hitherto, are lowly biodegradable substances highly apt to accumulate in the living body. There are fears about toxicity of these fluorochemicals to reproduction and growth although the degree of the toxicity is low. An industrial advantage of the fluorochemical according to the invention is that it is a substance safer for the environment.

[0140]

The amount of those fluoroaliphatic-group-containing monomers represented by general formula (2) to be incorporated in the fluoropolymer for use in the invention is generally 5% by mole or larger, preferably from 5 to 70% by mole, more preferably from 7 to 60% by mole, based on all monomers for the fluoropolymer.

The amount of the poly(oxyalkylene) acrylate and/or poly(oxyalkylene) methacrylate which is an essential ingredient in the invention is generally 10% by mole or larger, preferably from 15 to 70% by mole, more preferably from 20 to 60% by mole, based on all monomers for the fluoropolymer.

The amount of the monomer represented by general formula (2b) to be used for a preferred embodiment of the fluoropolymer for use in the invention is generally 3% by mole or larger, preferably from 5 to 50% by mole, more preferably from 10 to 40% by mole, based on all monomers for the fluoropolymer.

[0141]

The weight-average molecular weight of the fluoropolymer to be used in the invention is preferably from 3,000 to 100,000, more preferably from 6,000 to 80,000.

[0142]

The fluoropolymer to be used in the invention is added preferably in an amount in the range of from 0.001 to 10% by weight, preferably from 0.001 to 5% by weight, more preferably from 0.01 to 2% by weight, especially preferably from 0.01 to 1% by weight, based on the photosensitive composition (coating ingredients excluding the solvent).

[0143]

The fluoropolymer according to the invention can be produced by a known or common method. For example, the polymer can be produced by polymerizing monomers such as, e.g., a (meth)acrylate having any of the aforementioned fluoroaliphatic groups and a (meth)acrylate having a poly(oxyalkylene) group in an organic solvent with the aid of a general-purpose free-radical polymerization initiator. Alternatively, one or more other addition-polymerizable unsaturated compounds also may be added according to need to conduct polymerization in the same manner as described above to produce the target polymer. The dropping polymerization method in which monomers are polymerized while dropping the monomers and an initiator into a reaction vessel according to the polymerizability of

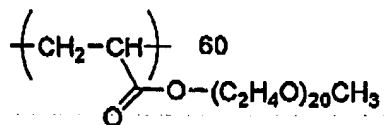
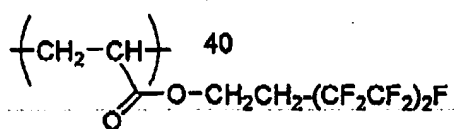
each monomer is effective in obtaining a polymer having an even composition.

[0144]

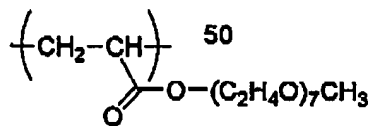
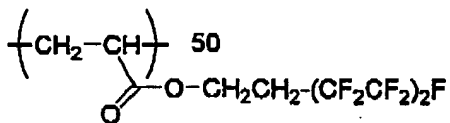
Examples of the structure of the fluoropolymer according to the invention are shown below, but the fluoropolymer should not be construed as being limited to these examples. In each formula, the numeral suffixed to each monomer unit indicates the molar proportion of the unit. Mw represents weight-average molecular weight.

[0145]

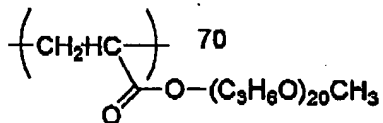
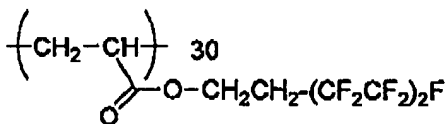
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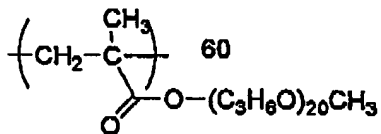
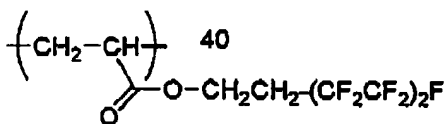
P-1
Mw 15,000



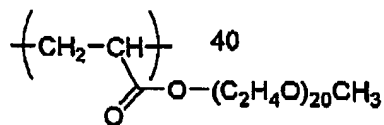
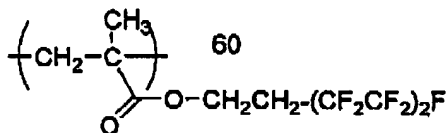
P-2
Mw 15,000



P-3
Mw 8,000



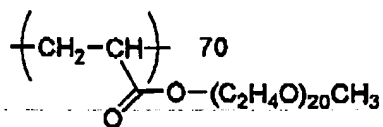
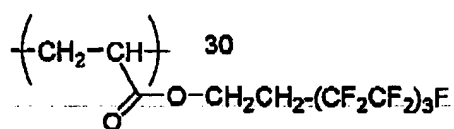
P-4
Mw 30,000



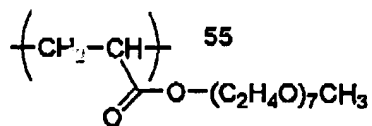
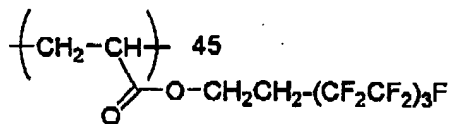
P-5
Mw 20,000

[0146]

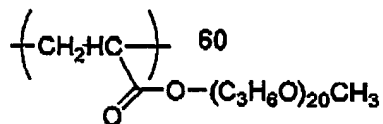
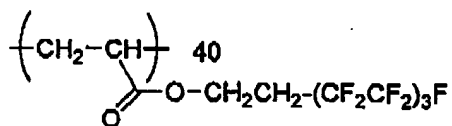
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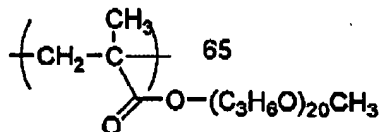
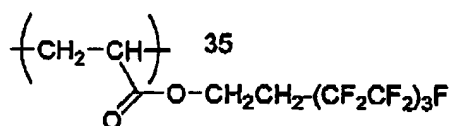
P-6
Mw 15,000



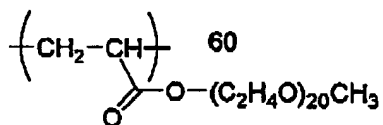
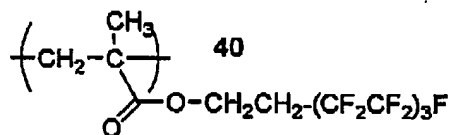
P-7
Mw 15,000



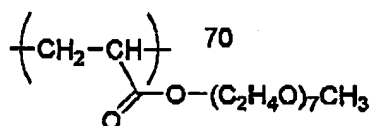
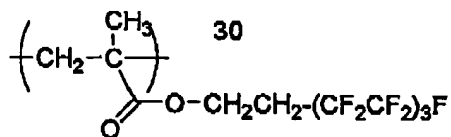
P-8
Mw 7,000



P-9
Mw 20,000



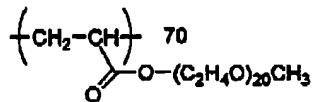
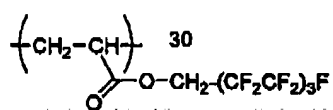
P-10
Mw 15,000



P-11
Mw 8,000

[0147]

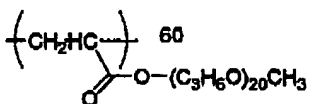
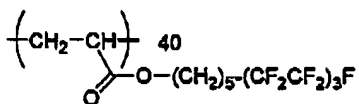
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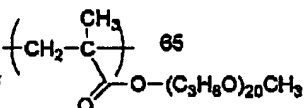
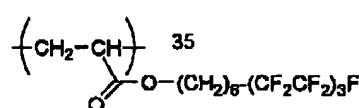
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Mw 15,000

[0148]

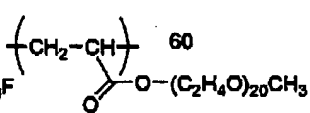
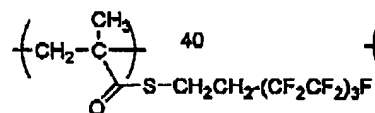
[Ka-58]



P-13
Mw 29,000



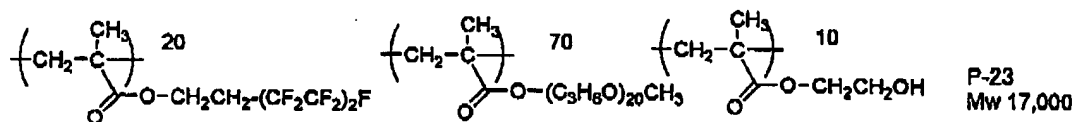
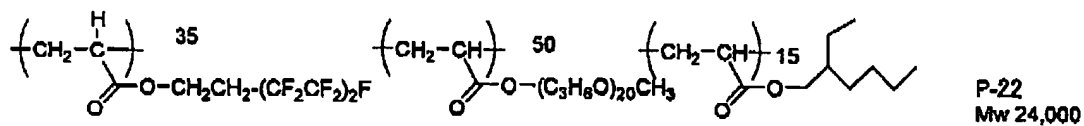
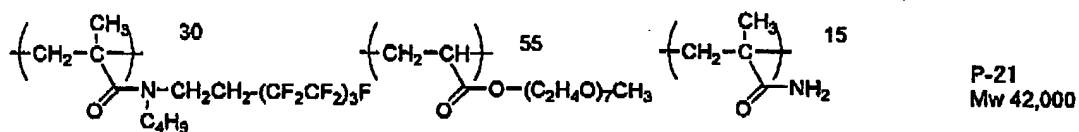
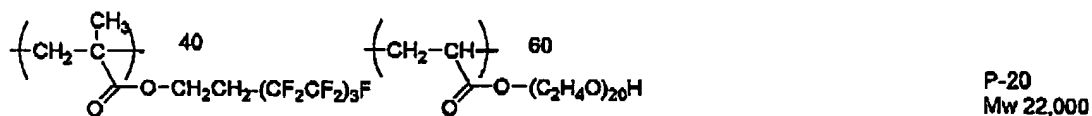
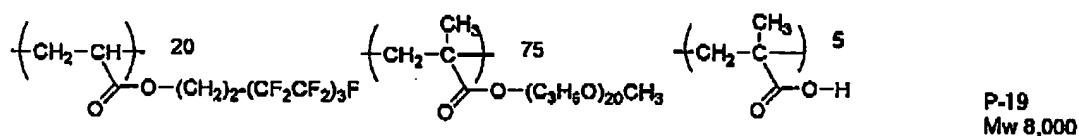
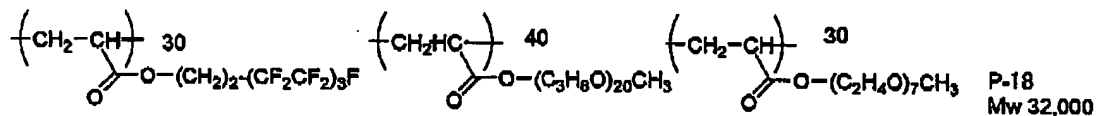
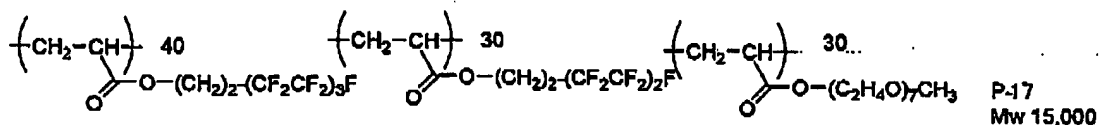
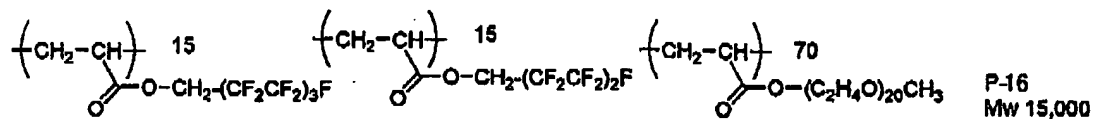
P-14
Mw 5,000



P-15
Mw 32,000

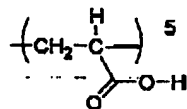
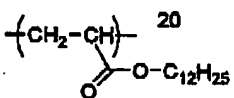
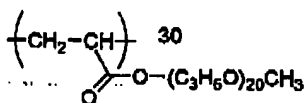
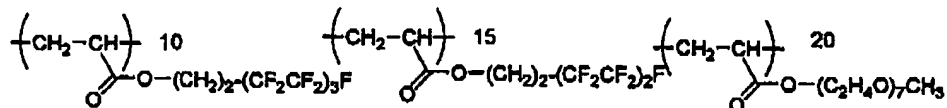
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[Ka-59]



[0150]

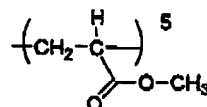
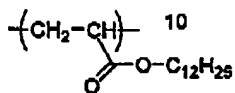
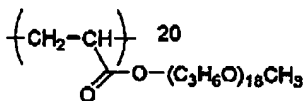
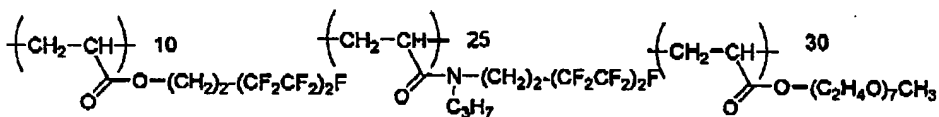
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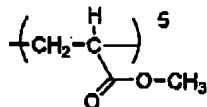
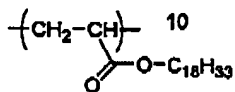
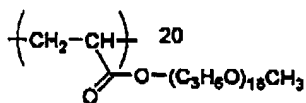
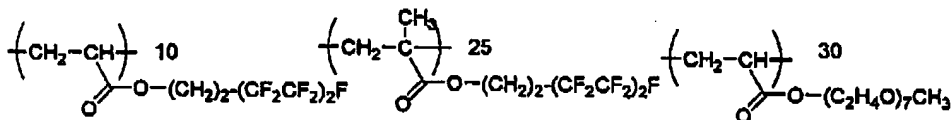
P-24
Mw 15,000

[0151]

[Ka-61]



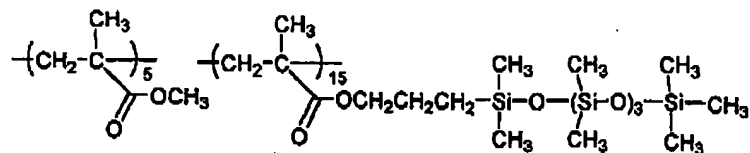
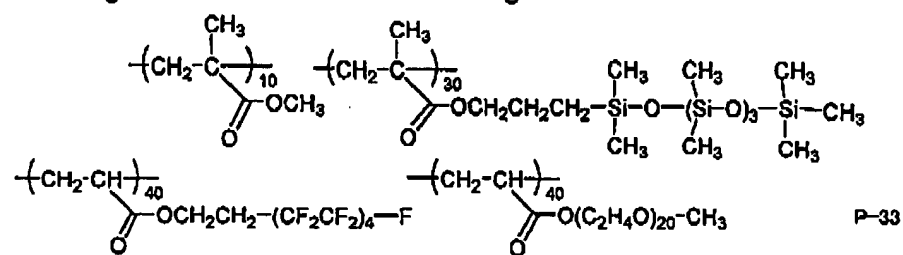
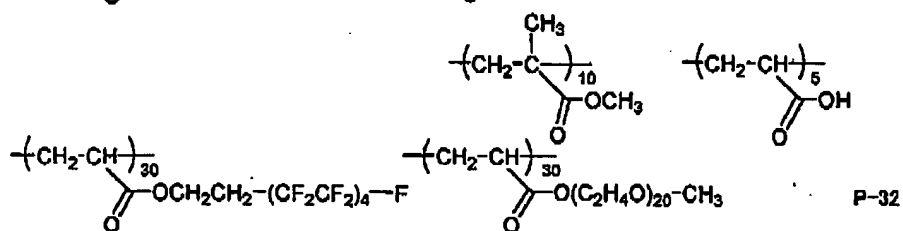
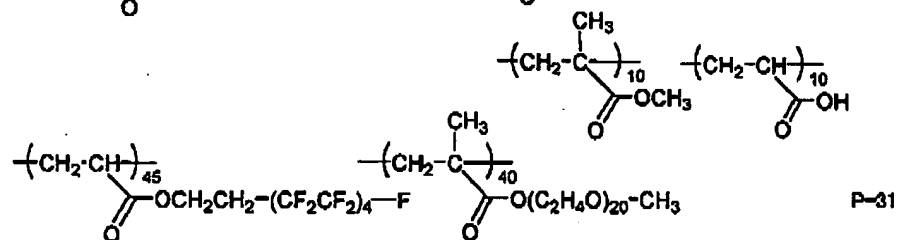
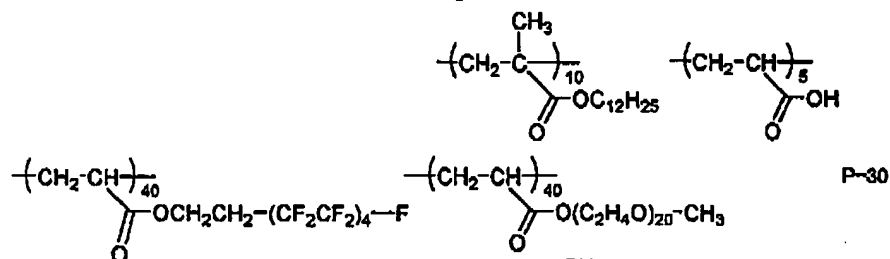
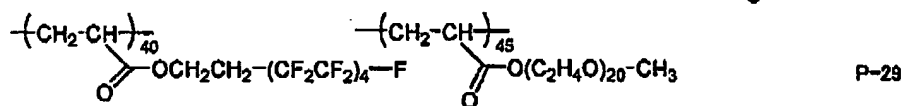
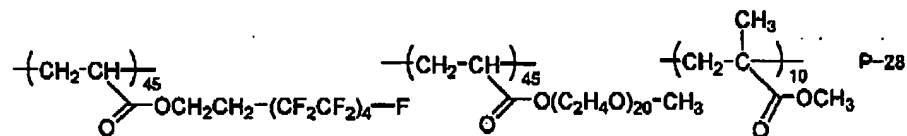
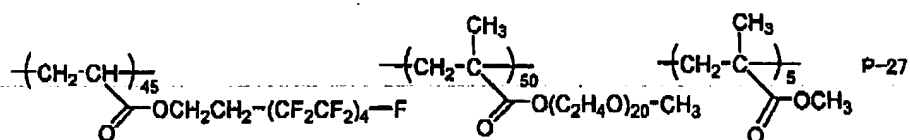
P-25
Mw 31,000



P-26
Mw 12,000

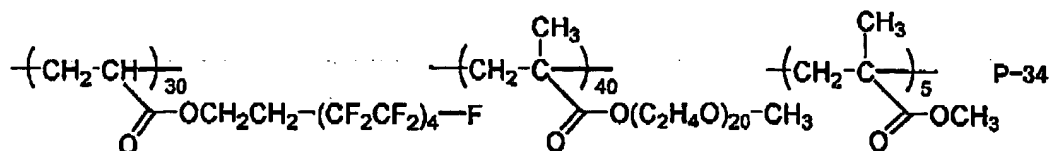
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[Ka-62]

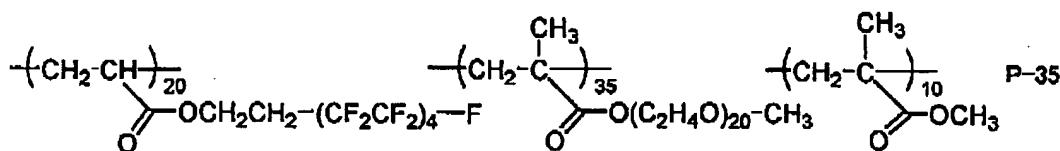
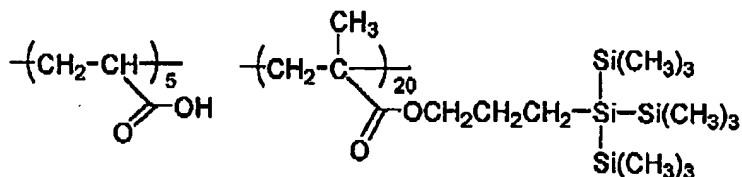


[0153]

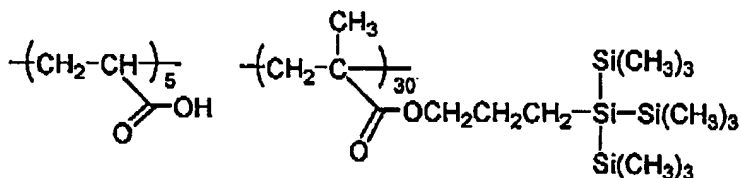
[Ka-63]



P-34



P-35



[0154]

[5] An organic basic compound can be used in the composition of the invention. Incorporation of this compound is preferred because it further improves storage stability and is effective in further reducing the line width change occurring with time after exposure (PED).

Preferred organic basic compounds usable in the invention are compounds having higher basicity than phenol. Especially preferred of these are nitrogen-containing basic compounds.

Examples of preferred chemical environments include the following structures (A) to (E).

[0155]

[Ka-64]

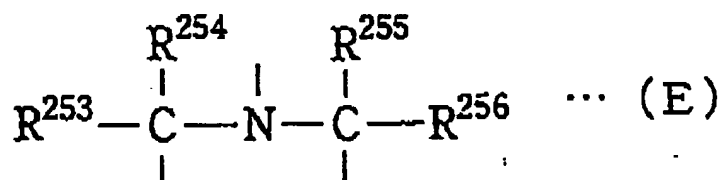


[0156]

In formula (A), R^{250} , R^{251} , and R^{252} may be the same or different and each are a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an aminoalkyl group having 1 to 10 carbon atoms, a hydroxyalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, provided that R^{251} and R^{252} may be bonded to each other to form a ring.

[0157]

[Ka-65]



[0158]

(In formula (E), R^{253} , R^{254} , R^{255} , and R^{256} may be the same or different and each represent an alkyl group having 1 to 6 carbon atoms.)

[0159]

More preferred compounds are cycloalkylamines containing one or more cycloalkyl groups, nitrogen-containing cyclic compounds (referred to also as cyclic amine compounds), and nitrogen-containing basic compounds having per molecule two or more nitrogen atoms differing in chemical environment.

[0160]

Preferred examples of the cycloalkylamines containing

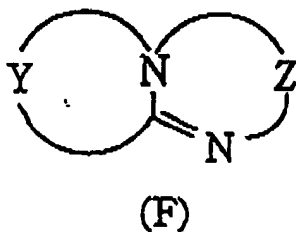
a cycloalkyl group include cyclopropylamine, cyclobutylamine, cyclopentylamine, dicyclopentylamine, dicyclopentylmethylaniline, dicyclopentylethylaniline, cyclohexylaniline, dimethylcyclohexylaniline, dicyclohexylaniline, dicyclohexylmethylaniline, dicyclohexylethylaniline, dicyclohexylbutylaniline, cyclohexyl-t-butylaniline, cycloheptylaniline, cyclooctylaniline, 1-adamantanamine, 1-dimethylaminoadamantane, 1-diethylaminoadamantane, 2-adamantanamine, 2-dimethylaminoadamantane, 2-aminonorbornene, and 3-noradamantanamine.

[0161]

The cyclic amine compounds more preferably are ones having a polycyclic structure. Preferred examples of the cyclic amine compounds include compounds represented by the following general formula (F).

[0162]

[Ka-66]



[0163]

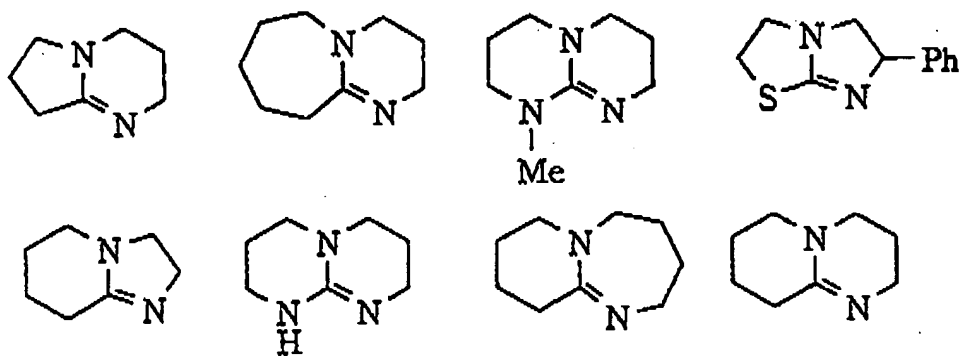
In formula (F), Y and Z each independently represent a linear, branched, or cyclic alkylene group which may contain

one or more heteroatoms and may be substituted.

Examples of the heteroatoms include nitrogen, sulfur, and oxygen atoms. The alkylene group is one having preferably 2 to 10, more preferably 2 to 5 carbon atoms. Examples of the substituents of the alkylene group include alkyl group having 1 to 6 carbon atoms, aryl groups, alkenyl groups, halogen atoms, and halogen-substituted alkyl groups. Specific examples of the compounds represented by general formula (F) include the following compounds.

[0164]

[Ka-67]



[0165]

Especially preferred of these are

1,8-diazabicyclo[5.4.0]undec-7-ene and

1,5-diazabicyclo[4.3.0]non-5-ene.

[0166]

The nitrogen-containing basic compounds having per molecule two or more nitrogen atoms differing in chemical environment especially preferably are compounds containing

both a substituted or unsubstituted amino group and a cyclic structure containing one or more nitrogen atoms or are compounds having an alkylamino group. Preferred examples thereof include substituted or unsubstituted guanidine, substituted or unsubstituted aminopyridine, substituted or unsubstituted aminoalkylpyridines, substituted or unsubstituted aminopyrrolidine, substituted or unsubstituted indazole, substituted or unsubstituted pyrazole, substituted or unsubstituted pyrazine, substituted or unsubstituted pyrimidine, substituted or unsubstituted purine, substituted or unsubstituted imidazoline, substituted or unsubstituted pyrazoline, substituted or unsubstituted piperazine, substituted or unsubstituted aminomorpholine, and substituted or unsubstituted aminoalkylmorpholines. Preferred substituents are amino, aminoalkyl groups, alkylamino groups, aminoaryl groups, arylamino groups, alkyl groups, alkoxy groups, acyl groups, acyloxy groups, aryl groups, aryloxy groups, nitro, hydroxy, and cyano.

[0167]

Especially preferred examples of these compounds include guanidine, 1,1-dimethylguanidine, 1,1,3,3-tetramethylguanidine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylaminopyridine, 4-dimethylaminopyridine, 2-diethylaminopyridine, 2-(aminomethyl)pyridine, 2-amino-3-methylpyridine,

2-amino-4-methylpyridine, 2-amino-5-methylpyridine,
2-amino-6-methylpyridine, 3-aminoethylpyridine,
4-aminoethylpyridine, 3-aminopyrrolidine, piperazine,
N-(2-aminoethyl)piperazine, N-(2-aminoethyl)piperidine,
4-amino-2,2,6,6-tetramethylpiperidine,
4-piperidinopiperidine, 2-iminopiperidine,
1-(2-aminoethyl)pyrrolidine, pyrazole,
3-amino-5-methylpyrazole,
5-amino-3-methyl-1-p-tolylpyrazole, pyrazine,
2-(aminomethyl)-5-methylpyrazine, pyrimidine,
2,4-diaminopyrimidine, 4,6-dihydroxypyrimidine, 2-pyrazoline,
3-pyrazoline, N-aminomorpholine, N-(2-aminoethyl)morpholine,
trimethylimidazole, triphenylimidazole, and
methyldiphenylimidazole. However, the basic compounds should
not be construed as being limited to these examples.

[0168]

Those nitrogen-containing basic compounds may be used alone or in combination of two or more thereof. The amount of the nitrogen-containing basic compounds to be used is generally from 0.001 to 10 parts by weight, preferably from 0.01 to 5 parts by weight, per 100 parts by weight of the positive photoresist composition (excluding the solvent).

In case where the amount of the nitrogen-containing basic compounds used is smaller than 0.001 part by weight, the effects described above cannot be obtained. On the other

hand, amounts thereof exceeding 10 parts by weight tend to result in reduced sensitivity and impaired suitability for development of unexposed areas.

[0169]

A surfactant, dye, pigment, plasticizer, photosensitizer, compound having two or more phenolic OH groups which enhances solubility in developing solutions, and the like can be incorporated into the chemical amplification type positive photoresist composition of the invention according to need.

[0170]

The positive photoresist composition of the invention preferably contains a surfactant.

Examples of the surfactant include nonionic surfactants such as polyoxyethylene alkyl ethers, e.g., polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether, and polyoxyethylene oleyl ether, polyoxyethylene alkylaryl ethers, e.g., polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether, polyoxyethylene/polyoxypropylene block copolymers, sorbitan fatty acid esters, e.g., sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate, and polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate,

polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate; fluorochemical surfactants such as F-Top EF301, FE303, and EF352 (manufactured by New Akita Chemical Company), Megafac F171, F173, F176, F189, and R08 (manufactured by Dainippon Ink & Chemicals, Inc.), Fluorad FC430 and FC431 (manufactured by Sumitomo 3M Ltd.), and Asahi Guard AG710 and Surflon S-382, SC101, SC102, SC103, SC104, SC105, and SC106 (manufactured by Asahi Glass Co., Ltd.); and other surfactants such as organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), acrylic or methacrylic (co)polymers Polyflow No. 75 and No. 95 (manufactured by Kyoeisha Chemical Co., Ltd.), and Troy Sol S-366 (manufactured by Troy Chemical Co., Ltd.).

Preferred of those surfactants are the fluorochemical or silicone surfactants from the standpoints of applicability and diminution of development defects.

[0171]

The amount of the surfactant to be incorporated is generally from 0.01 to 2% by weight, preferably from 0.01 to 1% by weight, based on all solid components of the composition of the invention.

Those surfactants can be used alone or in combination of two or more thereof.

[0172]

A spectral sensitizer such as those shown below may

be further added so that the photo-acid generator(s) used can be sensitive in a region of wavelengths which are longer than those of far ultraviolet and at which the photo-acid generators show no absorption. Thus, the chemical amplification type positive resist of the invention can be made sensitive to i- or g-line.

Preferred examples of the spectral sensitizer include benzophenone, p,p'-tetramethyldiaminobenzophenone, p,p'-tetraethylethylaminobenzophenone, 2-chlorothioxanthone, anthrone, 9-ethoxyanthracene, anthracene, pyrene, perylene, phenothiazine, benzil, Acridine Orange, benzoflavin, Setoflavine T, 9,10-diphenylanthracene, 9-fluorenone, acetophenone, phenanthrene, 2-nitrofluorene, 5-nitroacenaphthene, benzoquinone, 2-chloro-4-nitroaniline, N-acetyl-p-nitroaniline, p-nitroaniline, N-acetyl-4-nitro-1-naphthylamine, picramide, anthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone, 1,2-benzanthraquinone, 3-methyl-1,3-diaza-1,9-benzanthrone, dibenzalacetone, 1,2-naphthoquinone, 3,3'-carbonylbis(5,7-dimethoxycarbonylcoumarin), and coronene. However, the spectral sensitizer should not be construed as being limited to these examples.

[0173]

Examples of the compound having two or more phenolic OH groups which enhances solubility in developing solutions

include polyhydroxy compounds. Preferred examples of the polyhydroxy compounds include phenols, resorcinol, phloroglucinol, phloroglucide, 2,3,4-trihydroxybenzophenone, 2,3,4,4'-tetrahydroxybenzophenone, $\alpha, \alpha', \alpha''$ -tris(4-hydroxyphenyl)-1,3,5-triisopropylbenzene, tris(4-hydroxyphenyl)methane, tris(4-hydroxyphenyl)ethane, and 1,1'-bis(4-hydroxyphenyl)cyclohexane.

[0174]

When the chemical amplification type positive photoresist composition of the invention is used, the ingredients described above are dissolved in a solvent therefor and the resultant solution is applied to a substrate. Preferred examples of usable solvents include ethylene dichloride, cyclohexanone, cyclopentanone, 2-heptanone, γ -butyrolactone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, methyl methoxypropionate, ethyl ethoxypropionate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone, and tetrahydrofuran. These solvents may be used alone or as a mixture of two or more thereof.

[0175]

The chemical amplification type positive photoresist composition is applied to a substrate, such as ones for use in producing precision integrated-circuit elements (e.g., silicon/silicon dioxide coating), by an appropriate coating technique with, e.g., a spinner or coater. The resultant coating film is exposed to light through a given mask, subsequently baked, and then developed. Thus, a satisfactory resist pattern can be obtained.

[0176]

Examples of developing solutions for the chemical amplification type positive photoresist composition of the invention include aqueous solutions (usually from 0.1 to 10% by weight solutions) of alkalis such as inorganic alkalis, e.g., sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium phosphate, sodium metasilicate, and ammonia water, primary amines, e.g., ethylamine and n-propylamine, secondary amines, e.g., diethylamine and di-n-butylamine, tertiary amines e.g., triethylamine and methyldiethylamine, alcoholamines, e.g., dimethylethanolamine and triethanolamine, amides, e.g., formamide and acetamide, quaternary ammonium salts, e.g., tetramethylammonium hydroxide, trimethyl(2-hydroxyethyl)ammonium hydroxide, tetraethylammonium hydroxide, tributylmethylammonium hydroxide, tetraethanolammonium hydroxide, methyltriethanolammonium hydroxide,

benzylmethyldiethanolammonium hydroxide,
benzyl dimethylethanolammonium hydroxide,
benzyltriethanolammonium hydroxide, tetrapropylammonium
hydroxide, and tetrabutylammonium hydroxide, and cyclic amines,
e.g., pyrrole and piperidine.

[0177]

[Examples]

The invention will be explained below in greater detail
by reference to the following Examples, but the invention should
not be construed as being limited to these Examples.

[0178]

SYNTHESIS EXAMPLE 1 [Resin Synthesis Example]

Resin synthesis can be accomplished either by a method
using a vinyl ether for acetalization or by an acetal interchange
method using an alcohol and an alkyl vinyl ether.

Furthermore, a dehydrating azeotropic method such as
those shown below can be advantageously used for efficient
stable synthesis. However, these synthesis methods are mere
examples, and methods usable for synthesizing the resin according
to the invention should not be construed as being limited thereto.

[0179]

(1) (Synthesis of Resin 1)

VP 8000 (1,800 g), manufactured by Nippon Soda Co.,
Ltd., was mixed with propylene glycol monomethyl ether acetate
(PGMEA) (8,200 g) in a flask to obtain a solution. This solution

was distilled under reduced pressure to remove water and PGMEA through azeotropy.

After the water content was ascertained to have decreased sufficiently, a solution prepared by dissolving pyridinium p-toluenesulfonate (9.0 g) in cyclohexaneethanol (576.2 g) was added to the reaction mixture. t-Butyl vinyl ether (450.2 g) was further added thereto and the resultant mixture was stirred at room temperature for 5 hours.

To this reaction mixture were added water (3.6 L) and ethyl acetate (7.2 L). The resultant mixture was subjected to liquid separation, washing with water, and then vacuum distillation to remove the ethyl acetate, water, and PGMEA as an azeotrope component. Thus, an alkali-soluble resin having substituents according to the invention (resin 1) (30% PGMEA solution) was obtained.

GPC in terms of standard polystyrene revealed that the M_w of the polymer obtained was 11,000 and M_w/M_n therefor was 1.10.

[0180]

(2) (Synthesis of Resin 2)

VP 15000 (100 g), manufactured by Nippon Soda Co., Ltd., was mixed with propylene glycol monomethyl ether acetate (PGMEA) (400 g) in a flask to obtain a solution. This solution was distilled under reduced pressure to remove water and PGMEA through azeotropy.

After the water content was ascertained to have decreased sufficiently, ethyl vinyl ether (25.0 g) and p-toluenesulfonic acid (0.02 g) were added to the reaction mixture and this mixture was stirred at room temperature for 1 hour.

Triethylamine (0.03 g) was added to the reaction mixture to terminate the reaction. Water (400 mL) and ethyl acetate (800 mL) were added thereto. The resultant mixture was subjected to liquid separation, washing with water, and then vacuum distillation to remove the ethyl acetate, water, and PGMEA as an azeotrope component. Thus, an alkali-soluble resin having substituents according to the invention (resin 2) (30% PGMEA solution) was obtained.

GPC in terms of standard polystyrene revealed that the Mw of the polymer obtained was 18,000 and Mw/Mn therefor was 1.12.

[0181]:

(3) (Synthesis of Resin 3)

In 100 mL of acetone were dissolved 16.2 g of poly(p-hydroxystyrene) and isopropyl chloride. To this reaction mixture was added 1.8 g of triethylamine. This mixture was stirred at 50 to 55°C. for 5 hours. The resultant reaction mixture was transferred to 1,000 mL of water, and the upper layer was removed by decantation. The viscous resinous substance obtained was dissolved in 75 mL of acetone, and this solution was transferred to 500 mL of water. The rubbery resin

precipitated was dried under vacuum. Thus, 15.4 g of poly(p-hydroxystyrene/p-isopropoxystyrene) was obtained as a white powder.

The proportion of the p-hydroxystyrene structural units to p-isopropoxystyrene structural units in the polymer obtained was found to be 90:10 through ^1H -NMR spectroscopy. Furthermore, GPC in terms of standard polystyrene revealed that the weight-average molecular weight M_w of the polymer obtained was 15,500 and molecular-weight distribution M_w/M_n therefor was 1.12.

In 150 mL of ethyl acetate were dissolved 15.0 g of the poly(p-hydroxystyrene/p-isopropoxystyrene) and 3.0 g of ethyl vinyl ether. A catalytic amount of p-toluenesulfonic acid was added thereto. The resultant mixture was stirred at room temperature for 6 hours to allow a reaction to proceed.

After the reaction, the product of synthesis was neutralized with triethylamine and concentrated. The resultant viscous oily residue was dissolved in 100 mL of acetone. This solution was transferred to 3,000 mL of water in order to cause precipitation.

The polymer precipitated was taken out by filtration, washed with water, and vacuum-dried. Thus, 16.2 g of poly(p-1-ethoxyethoxystyrene/p-hydroxystyrene/p-isopropoxystyrene) was obtained as a white powder.

The proportion of the p-1-ethoxyethoxystyrene structural

units to p-hydroxystyrene structural units to p-isopropoxystyrene structural units in the polymer obtained was found to be 30:60:10 through ^1H -NMR spectroscopy. Furthermore, GPC in terms of standard polystyrene revealed that the Mw of the polymer obtained was 18,000 and Mw/Mn therefor was 1.12.

[0182]

(4) (Synthesis of Resin 4)

[SYNTHESIS EXAMPLE 4-1; Synthesis of Vinyl Ether]

Cyclohexylethyl alcohol was mixed with ethyl vinyl ether. Mercury acetate was added thereto and this mixture was stirred at room temperature for 12 hours. The resultant reaction mixture was extracted with ethyl acetate and water, and the extract was washed with water and then distilled under reduced pressure to obtain cyclohexylethyl vinyl ether (X-1) as the target compound.

[SYNTHESIS EXAMPLE 4-2]

In 100 mL of tetrahydrofuran were dissolved 39.6 g (0.225 mol) of p-tert-butoxystyrene monomer and 4 g (0.025 mol) of t-butylstyrene monomer which each had been dehydrated and distillation-purified in an ordinary manner. In a nitrogen stream, 0.033 g of azobisisobutyronitrile (AIBN) was added thereto with stirring at 80°C three times at an interval of 2.5 hours. After the final addition, the reaction mixture was continuously stirred for further 5 hours to conduct

polymerization reaction. The resultant reaction mixture was poured into 1,200 mL of hexane to precipitate a white resin.

The resin obtained was dried and then dissolved in 150 mL of tetrahydrofuran.

There to was added 4 N hydrochloric acid. The resultant mixture was heated with refluxing for 6 hours to hydrolyze the resin. This resin was reprecipitated from 5 L of ultrapure water, taken out by filtration, washed with water, and then dried. Furthermore, this resin was dissolved in 200 mL of tetrahydrofuran and the resultant solution was dropped into 5 L of ultrapure water with vigorous agitation to conduct reprecipitation. This reprecipitation operation was repeated three times. The resin obtained was dried in a vacuum dryer at 120°C for 12 hours. Thus, an alkali-soluble poly(p-hydroxystyrene/t-butylstyrene) copolymer resin R-2 was obtained.

The resin obtained had a weight-average molecular weight of 9,600.

[SYNTHESIS EXAMPLE 4-3]

The following ingredients were mixed together in a flask to obtain a solution.

Alkali-soluble resin R-2 obtained in Synthesis

Example 4-2

20 g

Propylene glycol monomethyl ether acetate (PGMEA)

80 mL

This solution was distilled under reduced pressure to remove water and PGMEA through azeotropy.

After the water content was ascertained to have decreased sufficiently, 5.0 g of the vinyl ether X-1 obtained in Synthesis Example 4-1 and 35 mg of p-toluenesulfonic acid were added to the reaction mixture. This mixture was stirred at room temperature for 1 hour, and triethylamine was added thereto to terminate the reaction.

Ethyl acetate was added to the reaction mixture. The resultant mixture was washed with water and then distilled under reduced pressure to remove the ethyl acetate, water, and PGMEA as an azeotrope component. Thus, an alkali-soluble resin having substituents according to the invention (resin 4) was obtained.

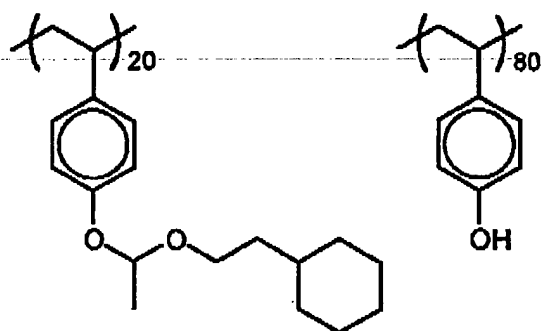
The resin obtained had a weight-average molecular weight of 11,000.

[0183]

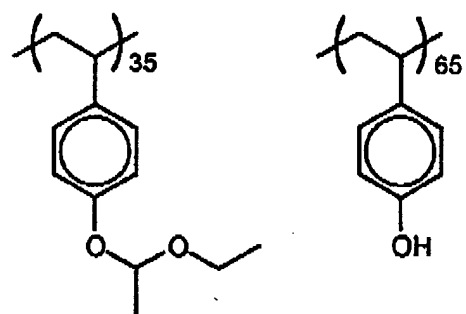
The structures of resins 1 to 4 described above are shown below. The proportion of repeating units in each resin shown below is given in molar ratio.

[0184]

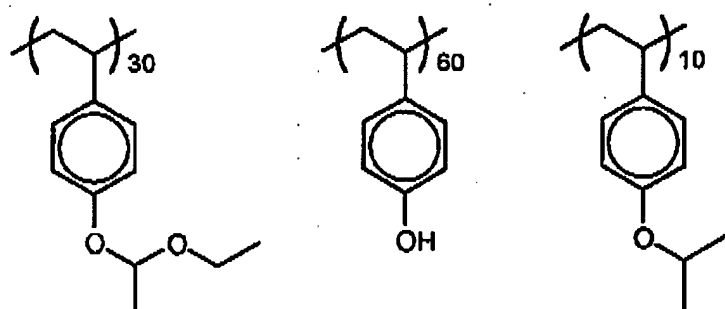
[Ka-68]



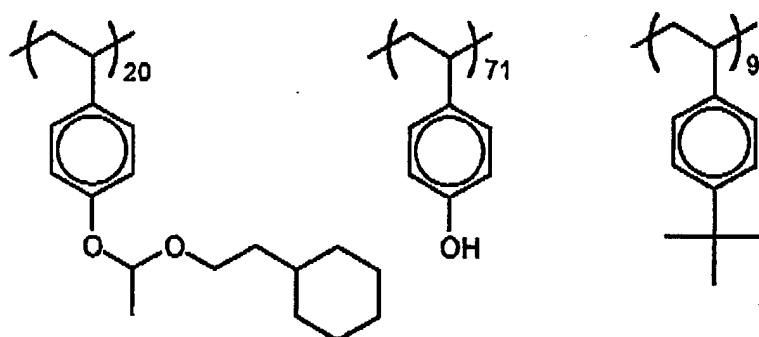
Resin 1



Resin 2



Resin 3



Resin 4

[0185]

[PHOTO-ACID GENERATOR SYNTHESIS EXAMPLE]

(1) (Synthesis of PAG1)

As PAG1 was used the compound described in the Example 86 of JP-A-2000-314956.

(2) (Synthesis of PAG2)

As PAG2 was used the compound described in the Example 9 of International Patent Publication No. 2000-517067.

[0186]

(3) Synthesis of Triphenylsulfonium

2,4,6-(Triisopropyl)phenylsulfonate Compound (PAG3)

In 300 mL of methanol was dissolved 17.5 g of triphenylsulfonium iodide. Thereto was added 10.9 g of silver oxide. This reaction mixture was stirred at room temperature for 4 hours and then filtered through a filter.

On the other hand, 14.7 g of 2,4,6-(triisopropyl)benzenesulfonyl chloride was dissolved in a mixture of 100 mL of methanol and 100 mL of water. A 10% methanol solution of tetramethylammonium hydroxide (TMAH) was added dropwise thereto with cooling with ice. The resultant mixture was reacted at 50°C for further 1 hour and then allowed to cool. Hydrochloric acid was added thereto to make the system acidic. This mixture was added to the reaction mixture obtained above, and the resultant mixture was stirred at room temperature.

Thereafter, the reaction mixture was concentrated and

chloroform was added thereto. This mixture was washed with TMAH twice and with water twice, and the resultant residue was concentrated. The solid obtained was recrystallized from diisopropyl ether/ethyl acetate. Thus, 22 g of the target compound (PAG3) was obtained.

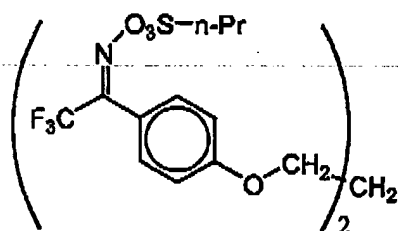
Various compounds were obtained in the same manner.

[0187]

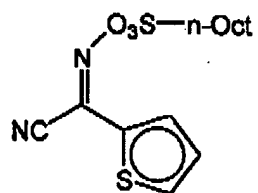
The structures of PAG1 to PAG6 described above are shown below.

[0188]

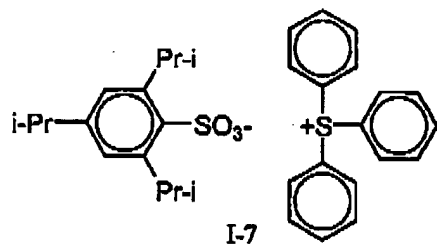
[Ka-69]



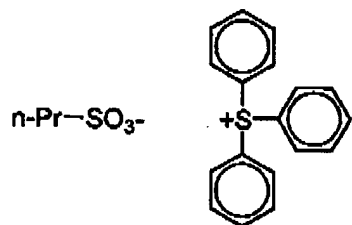
(PAG1)



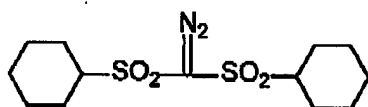
(PAG2)



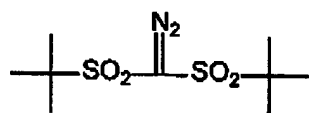
(PAG3)



(PAG4)



(PAG5)



(PAG6)

[0189]

[Synthesis of Fluororesin-Group-Containing Polymeric Compounds

(P-27, 28, 30, 34, and 35 shown above)]

Synthesis of P-27

Into a 500-mL glass reactor were introduced 23.3 g of F-66, 49 g of polyethylene monomer PE-1 shown below, 0.5 g of methyl methacrylate, and 0.25 g of dodecyl mercaptan. These ingredients were dissolved in 100 mL of MEK. After the solution was heated to 70°C, 0.3 g of azobisisobutyronitrile was added thereto to conduct a copolymerization reaction for 4 hours in a nitrogen atmosphere. Thereafter, 0.1 g of azobisisobutyronitrile was added thereto, and the resultant mixture was heated to 80°C and reacted for further 4 hours.

The resultant reaction mixture was distilled to remove the solvent therefrom and the residue was vacuum-dried. Thus, 70 g of a fluoroaliphatic-group-containing polymeric compound P-27 was obtained.

P-28, P-30, P-34, and P-35 were synthesized in the same manner as for P-27, except that the monomers shown in Table 1 were reacted in the respective amounts shown therein.

[0190]

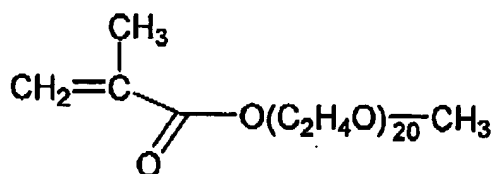
[Table 1]

Table 1

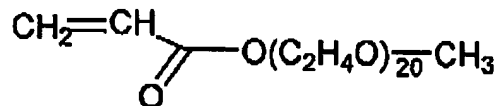
	Monomer 1	Monomer 2	Monomer 3	Monomer 4	Monomer 5
P-28	F-66 23.3 g	PE-2 43.5 g	methyl methacrylate 1.0 g		
P-30	F-66 20.7 g	PE-2 38.7 g	methyl methacrylate 1.0 g	acrylic acid 0.72 g	
P-34	F-66 15.5 g	PE-1 39.2 g	methyl methacrylate 0.5 g	acrylic acid 0.36 g	SI-1 7.2 g
P-35	F-66 10.4 g	PE-1 34.4 g	methyl methacrylate 1.0 g	acrylic acid 0.36 g	SI-1 10.8 g

[0191]

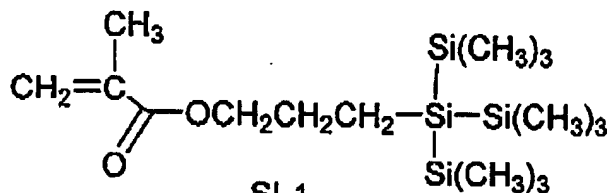
[Ka-70]



PE-1



PE-2



SI-1

[0192]

In propylene glycol monomethyl ether acetate (PGMEA solvent) were dissolved the ingredients shown in Table 2 or 3 in the weight ratio shown in the table so that the total concentration resulted in 12% by weight. The solution was filtered through a 0.1- μ m microfilter to prepare a positive photoresist.

Each resist fluid obtained was applied with a spin coater (Mark 8, manufactured by Tokyo Electron) to a silicon wafer on which a 110-nm coating film had been formed from an organic BARC (DUV 42) manufactured by Nissan Chemical Industries, Ltd.

The resist fluid applied was dried at 90°C for 90 seconds to form a 0.5- μ m resist film for evaluation.

[0193]

(Method of Development Defect Evaluation)

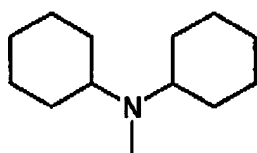
Without being patterned, each resist film for evaluation was heat-treated at 110°C for 90 seconds. This film was developed with 2.38% aqueous TMAH solution, subsequently rinsed, and then spin-dried to produce a wafer for development defect evaluation. The number of contaminant particles present on the surface of this wafer was counted with KLA-2113 (manufactured by KLA Corp.). The total particle number obtained by subtracting the number of dust-derived contaminant particles from the particle number counted was taken as the number of development defects.

[0194]

The following compound was incorporated as an additive in each of the resists obtained in the Examples and Comparative Examples, in an amount of 0.2 parts by weight.

[0195]

[Ka-71]



[0196]

[Table 2]

Table 2. Examples

	Alkali-soluble resin (parts by weight)	Photo-acid generator (parts by weight)			Fluoroaliphatic-group-containing polymeric compound (parts by weight)	Number of development defects
1	resin 1 (96.72)	PAG-1 (1.5)	PAG-4 (1.5)		P-27 (0.08)	20
2	resin 1 (96.72)	PAG-1 (1.5)	PAG-4 (1.5)		P-35 (0.08)	27
3	resin 2 (96.72)	PAG-1 (2.0)	PAG-3 (1.0)		P-27 (0.08)	22
4	resin 2 (96.72)	PAG-1 (2.0)	PAG-3 (1.0)		P-28 (0.08)	26
5	resin 2 (96.72)	PAG-1 (2.0)	PAG-3 (1.0)		P-30 (0.08)	33
6	resin 2 (96.76)	PAG-1 (2.0)	PAG-3 (1.0)		P-35 (0.04)	22
7	resin 2 (96.72)	PAG-1 (2.0)	PAG-3 (1.0)		P-35 (0.08)	21
8	resin 2 (96.64)	PAG-1 (2.0)	PAG-3 (1.0)		P-35 (0.16)	20
9	resin 2 (95.72)	PAG-1 (1.0)	PAG-3 (1.0)	PAG-5 (2.0)	P-35 (0.08)	34
10	resin 3 (94.72)	PAG-1 (4.0)	PAG-3 (1.0)		P-34 (0.08)	16
11	resin 4 (95.72)	PAG-1 (1.0)	PAG-3 (1.0)	PAG-5 (2.0)	P-30 (0.10)	18
12	resin 4 (94.8)	PAG-1 (1.0)	PAG-3 (1.0)	PAG-5 (2.0)	P-35 (1.0)	15
13	resin 4 (94.72)	PAG-2 (1.0)	PAG-4 (2.0)	PAG-6 (2.0)	P-34 (0.08)	29
14	resin 4 (93.6)	PAG-2 (1.0)	PAG-4 (2.0)	PAG-6 (2.0)	P-28 (1.2)	38

[0197]

[Table 3]

Table 3. Comparative Examples

	Alkali-soluble resin (parts by weight)	Photo-acid generator (parts by weight)			Fluoroaliphatic-group-containing polymeric compound (parts by weight)	Number of development defects
1	resin 1 (96.72)	PAG-1 (1.5)	PAG-4 (1.5)			202
2	resin 1 (96.72)	PAG-1 (1.5)	PAG-4 (1.5)			305
3	resin 2 (96.72)	PAG-1 (2.0)	PAG-3 (1.0)			750
4	resin 2 (95.72)	PAG-1 (1.0)	PAG-3 (1.0)	PAG-5 (2.0)		623
5	resin 3 (94.72)	PAG-1 (4.0)	PAG-3 (1.0)			804
6	resin 4 (95.72)	PAG-1 (1.0)	PAG-3 (1.0)	PAG-5 (2.0)		250
7	resin 4 (94.72)	PAG-2 (1.0)	PAG-4 (2.0)	PAG-6 (2.0)		286

[0198]

The results given in Tables 2 and 3 clearly show that the compositions according to the invention were exceedingly reduced in development defects.

[0199]

[Advantage of the Invention]

According to the invention, a positive photoresist composition effective in considerably diminishing development defects can be provided.

[Designation of Document] Abstract

[Abstract]

[Problem] To provide a positive photoresist composition effective in considerably diminishing development defects.

[Means for Resolution] A positive photoresist composition which comprises (A) an oxime sulfonate compound, (B) a resin having specific structural units and decomposing by the action of an acid to come to have enhanced solubility in an alkaline developing solution, and (C) a fluoroaliphatic-group-containing polymeric compound.

[Selected Drawing] None

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